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DEPARTMENT OF AGRICULTURE.
DIVISION OF CHEMISTRY.
BULLETIN No. 7.

METHODS OF ANALYSIS

OF

COMMERCIAL FERTILIZERS.

PROCEEDINGS

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

SEPTEMBER 1 AND 2, 1885.

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LETTER OF TRANSMITTAL.

WASHINGTON, D. C., *November* 7, 1885.

SIR: I transmit herewith a report of the proceedings of the second annual meeting of the Association of Official Agricultural Chemists, held at the Department building September 1 and 2, 1885.

The especial object of this meeting was to agree upon a uniform method of analysis of commercial fertilizers which could be practiced by official chemists in all parts of the country. This, however, is not the sole object of the Association, and its further scope was outlined by you in your address, which is contained in the inclosed proceedings.

In harmony with the purposes of the Department as set forth in the proceedings of the convention of delegates from agricultural colleges and experiment stations called by you in July last, I submit this record of the work of the Association of Chemists, feeling assured that by its approval and publication you will promote and foster that unity of action in matters pertaining to scientific agriculture which is necessary to its proper advancement.

Respectfully,

H. W. WILEY,

Chemist, and President of Association of Official Agricultural Chemists.

Hon. NORMAN J. COLMAN,

Commissioner.

ANALYSES OF COMMERCIAL FERTILIZERS.

PROCEEDINGS OF THE SECOND ANNUAL MEETING OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, AT WASHINGTON, D. C., SEPTEMBER 1, 1885.

Edited by CHARLES W. DABNEY, Jr., Ph. D., *North Carolina Agricultural Experiment Station, Secretary.*

MORNING SESSION, TUESDAY.

Through the courtesy of the honorable Commissioner of Agriculture, the Association assembled in the library of the Department of Agriculture, at 11 o'clock, Tuesday, September 1, 1885. In the absence of President Johnson, Prof. H. C. White, the vice-president, called the meeting to order.

Upon a call of the roll the following members were found to be present:

Chazal, P. E., State chemist South Carolina, Columbia.
Dabney, C. W., jr., Director North Carolina Experiment Station, Raleigh.
Gascoyne, W. J., Virginia Department of Agriculture, Richmond.
Jenkins, E. H., Commissioner Agricultural Experiment Station, New Haven.
Moses, W. E., Tennessee Department of Agriculture, Knoxville.
Richardson, Clifford, United States Department of Agriculture, Washington.
Stubbs, William C., State chemist Alabama, Auburn (removed to Sugar Experiment Station, New Orleans, La.).
White, H. C., State chemist Georgia, Athens.
Wiley, H. W., Chemist United States Department of Agriculture, Washington.

The following visiting analytical chemists were admitted to the privileges of the floor, under article 2 of the constitution:

Professor F. W. Clarke, Chemist, United States Geological Survey, Washington.
Mr. Thomas S. Gladding, New York.
Mr. Edgar Richards,
Mr. A. E. Knorr,
Mr. W. B. Price,
Mr. F. V. Broadbent,
Dr. C. A. Crampton,
} Assistant chemists of the Department of Agriculture.

Mr. A. De Ghequier, secretary of the American Fertilizer Association and of the Baltimore Chemical Exchange, was invited to a seat with the Association.

Dr. Jenkins, from the executive committee, reported an order of business for the meeting as follows:

(1) Reports of committees: (*a*) on phosphoric acid, (*b*) on potash, (*c*) on nitrogen; the reports to be received and discussed in this order.

(2) Determining methods to be used during the next year, in the same order.

(3) Election of officers.

(4) Miscellaneous business.

Adopted.

Dr. Dabney moved that a committee of three be appointed to invite the Hon. N. J. Colman, Commissioner of Agriculture, to meet them at some hour agreeable to him and make them an address.

Carried.

The Chair appointed Messrs. Dabney, Stubbs, and Jenkins as the committee.

After waiting upon the Commissioner, the committee reported that the honorable gentleman had consented to meet the Association and address them at 2.15 p. m., which became accordingly the order for that hour.

(1) *REPORTS OF COMMITTEES.*

(*a*) ON PHOSPHORIC ACID.

Dr. Jenkins, chairman, presented the report of the committee on phosphoric acid.

As required by the constitution of the Association, the committee on phosphoric acid herewith presents its report. The report covers (1) a brief notice of new analytical methods proposed for determining phosphoric acid; (2) a report of some work done during the past year by the committee and members of the Association; and (3) recommendations for the next year.

Henry Pemberton, jr. (Jour. of Franklin Inst., Chem. News, 46, and cited in Fres. Zeitschr. für Analyt. Chem., xxiii, 69), determined phosphoric acid volumetrically. A solution of ammonium molybdate of known strength is added to the phosphate solution till the phosphoric acid is completely removed.

Eighty-nine and five hundred and forty-three one-thousandths grams of ammonium molybdate are dissolved in one liter of water. If necessary to secure a clear solution, a little ammonia is added before filling up to the liter mark. One cubic centimeter of this standard solution corresponds to .003 grams of P_2O_5, since under the conditions here to be given the yellow precipitate will contain phosphoric acid and molybdic acid in the ratio of 1 : 24.

The P_2O_5 (about .1 gram, or at most 0.15 gram) should be in solution in nitric acid and free from organic matter and silica.

The concentrated solution, in a beaker of 100 to 125 c. c. capacity, is neutralized as nearly as possible, and to it are then added 2 c. c. of nitric acid, of specific gravity 1.4, and 10 grains of crystallized ammonium nitrate. The solution is heated to 60° C., and the standard molybdic solution is run in, with constant stirring, till all the P_2O_5 is separated.

To determine this point of complete separation the author, after each addition, filters a small quantity, heats to 60° C., and observes whether adding more of the standard solution produces a further precipitation. From the number of cubic centimeters used .5 c. c. is deducted, that being the amount which experiments have shown is necessary in excess to secure perfect precipitation.

Otto Freiherr von der Pfordten (Inaugural-dissertation, Fres. Zeitschr. für Analyt. Chem., xxiii, 422) proposes a volumetric method for the determination of P_2O_5. He secures the precipitation of ammonium phospho-molybdate without free molybdic acid in it. By zinc and hydrochloric acid he reduces the combined molybdic acid of the precipitate to the suboxide Mo_5O_7, which in the air at once passes into the sesquioxide Mo_2O_3, and then by a standard solution of potassium permanganate he determines the amount of oxygen necessary to oxidize the Mo_2O_3 to molybdic acid. From this the amount of phosphoric acid can be reckoned.

The details of the method are as follows: Phosphoric acid is precipitated as ammonium phospho-molybdate. Particulars with regard to the precipitation are not given in the abstract, but no doubt the method employed by Pemberton, which has been already described, will answer here. The precipitate is washed out on the filter pump with a nearly saturated solution of ammonium sulphate, until a drop of the filtrate no longer shows a dark brown coloration when ammonium sulphide is added to it. The precipitate is dissolved in a small quantity of ammonia, the solution is brought to a definite volume, and an aliquot part is taken which should contain not more than .3 gram MoO_3. In any case not more than 30 c. c. should be used; otherwise the solution is too dilute. To this solution in a small flask are added 50–60 c. c. 27 per cent. HCl and 8–10 grams of zinc in stick form, whose content of iron has already been determined by titration. When the solution has a yellow color the flask is cooled before all the zinc is exhausted, and its contents are rinsed into a porcelain dish containing 40 c. c., dilute H_2SO_4 and 20 c. c. of a solution of 200 grams $MgSO_4$ in one liter. The solution is at once diluted with water to 500 c. c. and titrated with a standard solution of potassium permanganate. From the number of cubic centimeters required for oxidation must be deducted the amount used in the oxidation of the iron which may exist as an impurity in the zinc.

an der Pfordten finds in the yellow precipitate the same relation (1 : 24) between P_2O_5 and M_oO_3 that was found by Finkner and H. Pemberton, jr.

The ammonia and water contents of the precipitate are variable.

C. Morh (Zeitschr. für Analyt. Chem., xxiii, 487) describes a method for the extraction of "reverted" P_2O_5 by means of an alkaline ammonium-citrate solution, and subsequent determination of the soluble and reverted together by the molybdate method, after oxidizing the organic matter with fuming nitric acid. This has at present no special interest for us, since the method of extraction is so entirely different from the one adopted by this Association.

David Lindo (Chem. News, xxxviii, 1884, 247, cited in Biedermann's Centralblatt für Ag. Chem., 1884, 642), by careful experiments, shows the value of his so-called "oxalate method," which consists in removing CaO as oxalate in a neutral solution of the phosphate, after separating silica, and then precipitating P_2O_5 by magnesia mixture with the addition of some citric acid. The method gives good results even where the iron oxide is present with silica; but if alumina is present with silica, the results will come too high.

Lindo also shows that the molybdate method in the presence of *small* amounts of silica will give accurate results, but not if a considerable quantity of SiO_2 is present. In one experiment the presence of .008 gram SiO_2 and .04 gram Al_2O_3 did not interfere with the accuracy of the determination.

J. S. Wells (Jour. Chem. Soc., 1885, 185, papers) proposes a method which is more rapid than the ammonium-molybdate method. He prepares two solutions:

A contains 900 grams of citric acid in 500 c. c. of water and 1,400 c. c. of ammonia solution, specific gravity .92.

B is a strong solution of magnesium citrate.

One gram of the fertilizer is fused with 3–4 grams of Na_2CO_3 and 3–4 grams $NaNO_3$. The fused mass is dissolved in nitric acid and filtered. To this phosphate solution is added enough of A to prevent any precipitation of phosphates when the solution is made alkaline. This usually requires about 10 c. c.

After making it alkaline the whole is allowed to stand thirty minutes. If any silica separates in that time it is filtered off. Then enough of B is added to precipitate all of the P_2O_5, and after stirring vigorously and allowing it to stand for some time the precipitate is filtered and weighed.

The author states with *naïveté* that if the phosphate is not fused too long the silica will remain insoluble, and "care must be taken not to mistake a possible precipitate of magnesic phosphate for one of silica."

John Ruffle (Chem. News, 51, 63) calls attention to the necessity of separating silica in all cases after boiling a phosphate with HCl, before precipitating with magnesia mixture. With the same phosphate he finds differences in some cases of nearly 1 per cent. of P_2O_5, de-

pending on whether SiO_2 has or has not been separated. The results come too high when the silica separation is omitted.

(It is not evident whether the "molybdate" method or the so-called "citric method" was used in the experiments reported.)

G. L. Spencer (Chem. Centr., 1884, 445; Jour. Chem. Soc., 1885, 436, abstracts) separates P_2O_5 by silver carbonate and determines it volumetrically by a solution of uranium acetate; 5–20 grams of the fertilizer are ignited till the ash is white, dissolved in strong HNO_3, diluted, filtered, and washed. By this means the larger part of the iron is separated and the chlorides are decomposed. To an aliquot part of the whole, which should contain from 0.1–0.5 gram P_2O_5, a slight excess of silver carbonate is added, which forms a perfectly insoluble precipitate of silver phosphate. This is boiled with the supernatant liquid, filtered and washed with boiling water, and then dissolved in a minimum quantity of HNO_3. The silver is thrown down by sodium chloride, the solution is neutralized with Na_2CO_3, and P_2O_5 is determined by uranium acetate.

J. Bougartz (Arch. Phar., 322, 846; Jour. Chem. Soc., 1885, 438, abstracts) states that P_2O_5, either free or combined with potash or soda, may be determined volumetrically by standard KOH or NaOH, using methyl orange or phenol-phthalein as an indicator.

If KOH is added to a solution of P_2O_5 till the red of methyl orange has changed to pale yellow, RH_2PO_4 is formed (112 parts KOH = 142 parts P_2O_5). If, now, phenol-phthalein is added, and the titration is continued till the red color appears, K_2HPO_4 is formed (112 parts K_2O = 142 parts P_2O_5). If H_2SO_4 or HCl is added till the methyl-orange red reappears, the titration may be repeated. If dicalcium phosphate is dissolved in HCl, and KOH is added till methyl orange becomes yellow, the solution then contains KCl, $CaCl_2$, and $CaHPO_4$ (?).

A further addition of the alkali till phenol-phthalein shows red gives tricalcium phosphate, dicalcium phosphate, and K_2HPO_4. $2\ CaH_4PO_4 + 6\ KHO + 2\ CaCl_2 = Ca_3(PO_4)_2 + 6\ H_2O + CaHPO_4 + K_2HPO_4 + 4\ KCl$. 168 parts KOH = 142 parts P_2O_5. If HCl is added, the titration may be repeated as before. In the presence of sufficient $CaCl_2$ monocalcic phosphate is entirely converted into tricalcium phosphate during the titration. 224 parts KOH = 142 P_2O_5.

By this method P_2O_5 may be readily estimated in manures: From the HCl solution iron and alumina are precipitated as phosphates by the addition of ammonia. Acetic acid is added to dissolve the calcium phosphate, and in a few minutes the precipitate is brought on a filter and washer till the acid reaction has disappeared.

The precipitate is dissolved in HCl and titrated. To the filtrate containing the rest of the P_2O_5 is added a little HCl and an excess of iron, aluminum and calcium chlorides. It is heated and the P_2O_5 preciptated by ammonia. The precipitate is brought on a filter, washed with water containing a little KOH, dissolved in HCl, and titrated after adding

excess of $CaCl_2$. It is necessary that the organic matter in the fertilizer should be entirely destroyed by calcination or fusion. The standard solution of KOH must be entirely free from alumina and carbonic acid. It is best prepared from $Ba(OH)_2$ and K_2SO_4.

C. Glaser (Fres. Zeitschr. für Analyt. Chem., 24, 178) describes a method depending on the precipitation of P_2O_5 by magnesia mixture in the presence of just enough ammonium citrate to prevent the separation of $Ca_3(PO_4)_2$, and of enough H_2SO_4 to combine with all the lime present.

There are required—

(1) Magnesia mixture prepared by dissolving 140 grams $MgSO_4$, 150 grams $(NH_4)_2SO_4$, and 30 grams NH_4Cl in 350 c. c. ammonia solution (16 per cent.) and 1,650 c. c. of water.

(2) A 50 per cent. solution of citric acid.

(3) Dilute ammonia, 250 c. c. (16 per cent. ammonia solution diluted to 1 liter).

(4) Dilute H_2SO_4 (100 c. c. of H_2SO_4, 60° B, diluted to 1 liter).

The phosphate solution in a beaker is neutralized until turbid, and just enough citric-acid solution is added to make it clear while still distinctly alkaline. This may require 3 c. c., or at most 4 c. c.

When cold the magnesia mixture is added dropwise, with constant stirring, and then ammonia in large excess. After six to eight, better twelve hours standing the precipitate is filtered, washed with dilute ammonia, and dissolved in H_2SO_4. More magnesia solution is added and the solution precipitated again with ammonia. The precipitate is filtered, washed, ignited, and weighed. The advantages claimed are rapidity, economy, and ease. The separation of SiO_2 is avoided and the results are absolutely accurate.

The same author compares the method used by this Association with the "oxalate method," and finds substantial agreement in the case of superphosphates which contain only a small amount of iron.

With natural phosphates and iron phosphates the agreement is not so good. The "oxalate method" used by him consists in bringing the filter and residue from the extraction of soluble P_2O_5 into a beaker and boiling for ten minutes with 100 c. c. of a solution of ammonium oxalate, which is saturated at ordinary temperatures. The solution is filtered and the residue washed with hot water.

We come now to the work which has been done during the year by members of the Association.

Last November your committee sent to eighteen official and commercial chemists two sealed samples of plain acid phosphates, one made from South Carolina rock and one from Navassa rock, and marked "South Carolina" and "Navassa." The material had been air-dried, put through a $\frac{1}{25}$-inch-mesh sieve, and very thoroughly mixed. The committee requested that determinations should be made, by the method recommended by this Association last year, of the following ingredients:

Water, soluble phosphoric acid, reverted phosphoric acid, and insoluble phosphoric acid.

In response to this request your committee has received reports from fifteen chemists. The number of laboratories represented is twelve, for in three cases reports were sent from chemists who worked in the same laboratory, presumably with the same reagents, &c.

These reports were received at different dates from December to the last of June. On July 1 the committee sent to each chemist who had participated in the work a tabulated statement of all the results which had been received. The names of the chemists were not given.

Some brief notice of these results may be in place here.

(1) The water determinations were absolutely worthless.

In "South Carolina" different chemists found from 8 to 10.50 per cent. moisture; in "Navassa" from 8.65 to 9.85 per cent.

This is to be expected. An accurate water determination in a superphosphate requires more time and care than the determination is generally worth. All superphosphates contain, besides hygroscopic moisture, water in combination with calcium sulphate, produced in their manufacture by the action of sulphuric acid on calcium phosphate. This water cannot be entirely expelled at 100° C., and only very slowly, if at all, at 110 to 120° C. Now, if organic matter such as is present in an ammoniated superphosphate is heated in air to 110 to 120°, it is more or less oxidized, and thus the accuracy of the determination is impaired.

To illustrate the uncertainty of the determination the following experiment made by the writer with "South Carolina" will suffice: Five portions, of 1 gram each, were dried for one, two, three, four, five hours, respectively, in an air-bath at 100° C. The results were as follows:

Mark.	Dried for—	Loss.
		Per cent.
A	1 hour	9.04
B	2 hours	8.86
C	3 hours	9.21
D	4 hours	9.20
E	5 hours	8.99

These results are tolerably uniform, but on continuing the drying the results were as follows:

	A.	B.	C.	D.	E.
For 6½ hours, total loss	9.49	9.71	9.59	9.32	9.12
For 6 hours additional, total loss	9.79	9.77	9.82	9.96	9.67
For 8 hours additional, total loss	10.02	9.92	10.12	10.15	10.02
For 10 hours additional at 110°, total loss	Lost.	10.29	10.37	10.30	10.07
For 6 hours additional at 110°, total loss	.....	10.39	10.37	10.30	10.27

Here the loss ceased, but if the superphospate had contained organic matter it is hardly to be expected that the results would have been as uniform.

(2) In the table below are given the average results of the fifteen analyses of "South Carolina" and "Navassa," with the highest and lowest figures reported:

	South Carolina.			Navassa.		
	Average.	Highest.	Lowest.	Average.	Highest.	Lowest.
Soluble, P_2O_5	12.01	12.74	11.59	7.26	8 08	6.40
Reverted, P_2O_5	2.25	2.88	1.75	3.83	5.10	2.92
Available, P_2O_5	14.26	14.78	13.73	11.09	11.82	10.58
Insoluble, P_2O_5	1.28	1.56	.78	5.93	6.37	5.17
Total, P_2O_5	15.54	16.12	15.09	17.02	17.72	16.31

The most important determinations are those of the available and the total phosphoric acid.

In "South Carolina" we notice a difference of about 1 per cent. between the highest and lowest determination of available P_2O_5, or a difference in extreme cases of $\frac{1}{2}$ per cent., from the mean of all results. In "Navassa" the difference between the highest and lowest results on available P_2O_5 is $1\frac{1}{4}$ per cent., or a difference running from 0.7 per cent. above the mean to 0.5 below the mean. The differences between the results of the determinations of total P_2O_5 are the same in "South Carolina" and a little larger in "Navassa" than the corresponding differences observed in the results on available P_2O_5.

The question now arises, Is the average results obtained by these fifteen chemists correct? The writer has endeavored to answer the question, with strong probability, by the following experiments in the case of the total P_2O_5.

The purity of the reagents used and accuracy of manipulation were tested as follows:

P_2O_5 was determined by ignition as pyrophosphate in a sample of finely pulverized "C. P." hydrogen sodium phosphate, which had been recrystallized and dried.

The per cent. of P_2O_5 was found to be: 26.39; 26.43; 26.46; 26.46. Average: 26.43.

P_2O_5 was next determined in the same salt by precipitation with magnesia mixture. The results were: 26.43; 26.35; 26.39; 26.42; 26.31. Average: 26.38, or 99.8 per cent.

In the same salt P_2O_5 was also determined by the molybdate method. The results were: 26.41; 26.41; 26.31; 26.29; 26.42. Average: 26.37, or 99.8 per cent.

Reagents and manipulation being satisfactory, determinations of total P_2O_5 were made in "South Carolina" and "Navassa" by the molybdate method. The solutions of the phosphates were prepared as follows:

(A) Fused from 0.5 to 1 gram phosphate with 7 grams sodium carbonate, dissolved the mass in water and HCl, separated SiO_2, and filtered.

(B) Digested the phosphate (0.6 to 0.5 grams) with 20 c. c. concentrated HCl, diluted, and filtered.

(C) Added to the phosphate (0.6 to 0.5 grams) about 7 c. c. saturated solution of Mg $(NO_3)_2$, evaporated to dryness, and ignited. Dissolved in 20 c. c. concentrated HCl, diluted, and filtered.

(D) Digested 0.5 with about 2 c. c. oil of vitriol at 100° C. for three to five hours, diluted, boiled residue with strong HCl, and filtered.

A was tried on acco unt of the suggestion of Dr. Shepard that in some cases pyrophosphate may be formed in a phosphate heap, which would not be recovered in the usual method of solution.

D was tried to expel fluorine, which occurs in some phosphates and is said to impair the accuracy of the molybdate method.

The results are given in the following table, followed by others contributed by Mr. Clifford Richardson, of the Department of Agriculture:

	South Carolina.	Navassa.
A	15.35	16.96
	15.45	16.85
B	15.51	16.80
	15.31	16.83
C	15.43	17.00
	15.37	16.93
D	15.22	17.00
	15.50	17.20
		16.98
Average	15.39	16.95
Ignited with Mg. $(NO_3)_2$; solution in HNO_3	15.48	17.27
Ignited with Mg. $(NO_3)_2$; solution in HCl	15.56	17.18
Ignited alone; solution in HCl	(15.59)	(16.87)
Not ignited; solution in HCl	15.26	17.26
Not ignited; solution in HNO_3	15.69	17.31
Average	15.49	17.25
Average of 15 analyses by official and commercial chemists	15.54	17.02

The writer considers the experiments here given as confirming the results obtained by other chemists, simply because they were made under varying conditions, while the others were made presumably under the same conditions.

The results obtained this year leave much to be desired. The samples, it is believed, were as nearly identical as it is possible to make them, and a nearer agreement between chemists on identical samples is necessary and attainable.

The subcommittee of the chemical trades section of the London Chamber of Commerce (Chem. News, 1884, p. 230) decided that for their uses a difference of less than 1½ per cent. of tricalcium phosphate (equivalent to about 0.7 per cent. P_2O_5) was admissible.

If differences of 1½ per cent. or more occurred the analysts concerned were to be requested to explain the discrepancy.

No determinations of available or total P_2O_5 in South Carolina and three in Navassa differ 0.7 per cent. from the mean of all results, but as between the highest and lowest figures there are many differences

of more than 0.7 per cent. Certainly a chemist who cares for his own reputation and for justice will not let a difference of 0.7 per cent. between his own and his neighbor's determination pass without assuring himself by a repetition of his own work and by examination of his reagents that his own result is veary nearly correct for the sample on which he worked.

In conclusion your committee recommends that the methods of analysis adopted at our last meeting be amended as follows:

Before the "determination of phosphoric acid in fertilizers" insert the following:

DETERMINATION OF MOISTURE IN FERTILIZERS.

(*a*) In potash salts, nitrate of soda, and sulphate of ammonia, heat 1 to 5 grams at 130° C. till the weight is constant, and reckon water from the loss.

(*b*) In all other fertilizers, heat 2 grams, or, if the sample is too coarse to secure uniform lots of 2 grams each, 5 grams for 5 hours at 100° in an air bath.

Your committee also recommends that the following description of the Association's method of determining "citrate insoluble phosphoric acid."

The method of extracting "reverted" phosphoric acid was originally designed for and is applicable only to superphosphates, plain or nitrogenized, and was not intended to be applied to rock phosphates, natural guanos, or any other non-acidulated materials to test their relative solubility or availability. In case, however, a determination of citrate insoluble phosphoric acid is required in these non-acidulated goods, it is to be made by treating 2 grams of the phosphatic material, without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, &c.), the residue insoluble in ammonium citrate is to be ignited with magnesium nitrate.

Your committee further recommends that in all other respects the method adopted at our last meeting for the determination of P_2O_5 in its three states be rigorously followed during the coming year.

They specially urge attention to the following points:

(1.) The solution of ammonium citrate to be strictly neutral and of the specific gravity indicated.

(2.) Perfect solution of the phosphate in acid. After boiling with acid, diluting, and decanting, it is well to boil the insoluble residue again with strong acid.

(3.) The magnesia mixture to be added not more rapidly than indicated (one drop per second). (Peitsch, Rohn & Wagner, Fres. Zeitschr. für analyt. Chem., xix, 448.)

Since the ignition with $Mg(NO_3)_2$ requires some time and an additional transfer of the material from one vessel to another, which always involves the possibility of mechanical loss, experiments are desirable to determine whether organic matter can be destroyed or made harmless by oxidation in the wet way, by fuming nitric acid or other reagents in the flask in which the subsequent solution of the phosphate is to be made.

It is also desirable to know to what extent silica passes into solution

when phosphates of various kinds are digested in strong acid. A single experiment on "South Carolina" gave the writer—

	Per cent.
Total sand and silica	3.92
Brought into solution by boiling in strong HCl	.02
Brought into solution by ignition with $Mg(NO_3)_2$ and solution in strong HCl	.05

It is also desirable to know what effect silica in solution has on the determination of P_2O_5 by the molybdate method. The testimony on this point is conflicting. (See Bertrand, Jahresber. Ag. chem., xxvi, 318; Lindo, Chem. News, xxxviii, 1884, 247 *et seq;* Bied. Centralbl. Ag. Chem., 1884, 642; Atkinson, Fres. Zeitschr. für analyt. Chem., xviii, 477; Jenkins, Jour. f. prakt. Chem., 13, 237.)

Your committee also express the belief that an annual distribution of samples and comparison of results will be of great use in securing accuracy and uniformity among analysts, and urge on the members of the Association the desirability of promptly analyzing and reporting results on samples which they receive.

All of which is respectfully submitted.

E. H. JENKINS.
Chairman.
H. C. WHITE.
W. C. STUBBS.

Mr. Gladding said a study of the results of the analyses just given, especially those of Dr. Jenkins and Mr. Richardson, shows that while working on acid phosphates made from Charleston and Navassa rock the results were practically indentical whether a simple solution in HCl or HNO_3, a fusion with Na_2CO_3, or an ignition with H_2SO_4 were employed. He therefore argued that, as the simplest manipulation was always to be preferred, other things being equal, the use of magnesium nitrate be omitted in all such cases, where it is, without dispute, unnecessary.

Dr. Dabney found the manipulation of the phosphate in a capsule with magnesium nitrate, as laid down in the adopted method, awkward and perilous. Fine cracks form in the capsules which are scarcely to be seen, but which let a little of the concentrated solution leak through at the next step. Like Mr. Gladding, and for these additional reasons, he had not treated simple rock phosphate with magnesium nitrate and ignited, except in making experiments and when the character of the phosphate was uncertain. He hoped the Association would recognize this as sufficient.

Dr. Jenkins said the reason why HCl was adopted by the Association as a solvent for phosphates, instead of HNO_3, was that it more readily and quickly brings them into solution. With care HNO_3 will answer perfectly. During an entire season a comparison was made of the two solvents in his laboratory by different chemists. In the rather small number of cases where there was disagreement the HCl solution invariably

gave slightly higher results. It may be claimed that this was due to silica brought into solution by the HCl. Two trials made with reference to this point showed that it dissolved silica very little, if at all. (.02 and .05 per cent. silica were dissolved from South Carolina phosphate, which contained 3.92 per cent. of sand and silica.) The presence of chlorides, introduced by hydrochloric acid, somewhat retards but does not prevent the precipitation of P_2O_5.

He believes the reduction of P_2O_5 to pyrophosphate during ignition of the insoluble residue from the citrate extraction is slight. He had at hand only the results of a single trial. Three such residues from a superphosphate containing animal matter were ignited directly, three others were fused with sodium carbonate, silica was separated, and P_2O_5 was determined in the six lots. The results were:

	Average.
Ignited: 2.82, 2.75, 2.91	2.83
Fused: 2.85, 2.96, 3.04	2.95

Mr. Gladding read the following paper, which was ordered to be spread upon the minutes:

ON THE DETERMINATION OF CITRATE-SOLUBLE PHOSPHORIC ACID IN NATURAL GUANOS.

By Thomas Gladding, A. M.

In the method adopted by the Association of Official Agricultural Chemists, at Philadelphia, 1884, for the estimation of the reverted or citrate-soluble P_2O_5 in superphosphates, 2 grams of the fertilizer are digested with 100 c. c. of the solvent.

This amount of solvent is regarded as ample for the solution of all strictly precipitated P_2O_5 that may be present. It undoubtedly at the same time dissolves a considerable portion of the strictly insoluble P_2O_5 that is contained in the superphosphate, but this is unavoidable, and as all superphosphates are treated exactly alike, no injustice is done by this course.

The agricultural chemist is frequently called upon, however, to determine the so-called available or citrate-soluble phosphoric acid in the many natural guanos that are in the market. These guanos have not been treated with acid and do not contain, strictly speaking, any reverted phosphate. What, then, it may be asked, is the object of determining the citrate soluble in these forms of fertilizer? Obviously there is only one object, and that is to determine their degree of solubility as compared with one another and with artificially treated manures.

In determining the citrate-soluble P_2O_5 in this form of fertilizer, the Association has not distinctly stated the amount of fertilizer that must be used to every 100 c.c. of citrate-solution. In consequence considerable latitude is exercised at the present time in this direction, some analysts employing 2 grams to 100 c.c. solvent, while others use the much smaller

quantity of 0.4 gram to 100 c.c. solvent, causing thereby much confusion and dissatisfaction.

The object of determining the available or citrate-soluble in these natural guanos is, as has been said, to furnish a means of comparison as to their relative solubility. Thus, in my paper "On the reversion of phosphoric acid" (Am. Chem. Journal, Vol. 6, No. 1), I found that by treating several guanos in the same way exactly (2 grams to 100 c. c. cit. sol.) I obtained as citrate-soluble, respectively:

	Per cent.
Oruba guano	2.09
Orchilla guano	4.81
Mona Island guano	6.82
Peruvian guano	13.14

This gives us at once a rough comparison of these guanos. Peruvian, for instance, is at least six times more easily soluble than Oruba guano.

Right here arises a strong objection to the use of 0.4 gram to 100 c. c. solvent, or rather two objections.

First. In the above tests all but a trace of the Peruvian guano was dissolved. Now had I used 0.4 gram of each, my results on the Peruvian would consequently be the same as above, for I could not dissolve out more than there is present, while the Orchilla would have come up to the same amount at least as the Peruvian, if not more, and the Oruba would probably give at least 6 or 7 per cent. As a result all sense of comparison would be lost and the comparative test be valueless. We may lay it down as an axiom: *A unit of comparison must not be greater than any one of the objects compared.*

Second. In the second place these guanos will inevitably be compared with superphosphates. Thus a large lot of Orchilla guano tested by using 0.4 gram to 100 c. c. citrate-solution gave total P_2O_5 16.42; available or citrate solution 13.05 per cent. An acid phosphate analyzed at the same time was reported as containing total P_2O_5 14.59; available, 10.94. Comparing these reports side by side we have:

	Acid phosphate.	Guano.
	Per cent.	*Per cent.*
Total P_2O_5	14.59	16.42
Available	10.94	13.05
Insoluble	3.65	3.37

In other words, the guano is a far more valuable article than the acid phosphate; a most erroneous conclusion.

But a direct argument for the use of 0.4 gram of these guanos to 100 c. c. solvent is made as follows:

Manufacturers mix these guanos with superphosphates in very small proportions, say 10 and 20 per cent. When, therefore, 2 grams of such mixture is digested with 100 c.c. solvent we are employing only 0.2 and 0.4 gram of the guano, respectively, to 100 c.c. citrate-solution. A much larger amount is dissolved than when 2 grams are used to 100 c.c. Consequently, when analyzing the guano before mixing with the acid phosphate the same amount, 0.4 gram, should be taken.

In answer to this argument, it is true that where 0.4 gram of such a guano is digested alone with 100 c. c. citrate-solution a very much larger percentage of P_2O_5 is dissolved than when 2 grams are thus treated. But when this 0.4 gram is mixed with 1.6 grams of a superphosphate, there remains, after washing out the soluble, a large amount of reverted and insoluble phosphates, as also a large amount of $CaSO_4$, organic matter, &c. Now in the presence of these foreign matters we have found that the action of the citrate on the $\frac{4}{10}$ gram of admixed guano is greatly weakened and is very nearly represented by the action on the 2 grams of guano when treated alone with 100 c.c. solution. For some years our firm has analyzed Orchillas, Curaçaos, &c., for available, using 2 grams and 100 c. c., for manufacturers. The mixtures of these guanos with acid phosphates have analyzed almost exactly what was expected by calculation from the analyses of the component parts.

To convince ourselves, however, on this point, we have taken a sample of Orchilla guano, mixed it with a superphosphate and analyzed mixture, with the following results:

Analysis of superphosphate. [2 grams to 100 c. c. cit. sol.]	*Per cent.*	*Analysis of guano.* [2 grams to 100 c. c.]	[.4 grams to 100 c. c.]
Total P_2O_5	11.55	16.42	16.42
Available P_2O_5	9.75	5.87	13.05
Insoluble P_2O_5	1.80	10.55	3.37
[First mixture.]		[Second mixture.]	
1.8 grams superphosphate. 0.2 gram guano = 10 per cent. guano. Insoluble obtained, 3.00 per cent.		1.6 grams superphosphate. 0.4 gram guano = 20 per cent. guano. 3.88 per cent.	

Caculating the theoretical results from analyses of components:

(1) When 2 grams guano were used to 100 c. c.:

[First mixture.]

	Per cent.		*Per cent.*	
1.8 grams superphosphate	×	1.8 insoluble ...	.0324	grams.
0.2 grams guano	×	10.55 insoluble ...	.0210	
			2). 0534	
			2.67	

[Second mixture.]

	Per cent.		*Per cent.*	
1.6 gram superphosphate	×	1.8 insoluble...	0.288	grams.
0.4 grams superphosphate	×	10.55 insoluble...	0.420	
			2). 0708	
			3.54	

That is, the insolubles actually obtained were 0.23 per cent., and 0.34 per cent. higher than they should have been by calculation, thus show-

ing that the availables in the guano were rather above than under the truth.

(2) When .4 grams guano were used to 100 c. c.:

[First mixture.]			Second mixture.		
	Per cent.			*Per cent.*	
1.8 grams superphosphate ×	1.8	.0324	1.6 grams superphosphate ×	1.8	.0288
0.2 grams guano ×	3.37....	.0067	0.4 grams guano ×	3.37 ...	.0134
		2).0391			2).0422
Insoluble.....		1.95			2.11

If we had reported this guano to the manufacturer as containing 13.35 per cent. available, 3.37 per cent. insoluble, he would have calculated on getting these last figures on his mixtures, viz, 1.95 and 2.11 per cent. When on analysis his mixtures actually returned 3 per cent. and 3.54 per cent. insoluble, an explanation would be in order. The above analyses were made just at the time of mixture. A mixture of 10 per cent. guano and 90 per cent. super. was allowed to stand four days. The sample was then analyzed, and even ground to a fine paste, instead of using a rubber pestle, as usual, so as to obtain as low an insoluble as possible. The analysis gave insoluble 2.80 per cent.

In conclusion, we believe the only just and safe course to be the employment in all cases of the same standard of measurement, the use of 2 grams of all classes of fertilizers to 100 c. c. of citrate solution.

To avoid difficulties arising from washing we use the following method: After digesting 30 minutes at 65° C. the flask is filled to the mark with water, cooled quickly, filtered till perfectly clear, an aliquot evaporated to dryness, ignited with magnesium nitrate to P_2O_5, estimated as usual. The reverted in superphosphates might be determined directly in the same way.

Laboratory of Stillwell and Gladding.

By consent of the Association, Prof. W. C. Stubbs read the following paper, by Mr. B. B. Ross, an assistant chemist in the laboratory of the Alabama State Chemist, and it was ordered to be spread upon the minutes.

METHOD OF DETERMINING CITRATE-SOLUBLE PHOSPHORIC ACID BY ELIMINATION OF CITRIC ACID.

This method depends upon the precipitation of citric acid in neutral solutions by addition of calcium chloride, the solution being heated nearly to boiling in order to render the precipitate insoluble in the ammonium chloride formed. In the determination of citrate-soluble phosphoric acid by this method, the method adopted by the Association is followed as far as the filtration of the ammonium citrate solution, in which the residue from the treatment with water has been digested for half an hour at 65° C.

The following scheme of analysis was followed in arriving at the appended results:

Carefully collect the filtrate and washings resulting from the ammonium citrate treatment; transfer to a cylinder and dilute to 200 c. c.; mix well.

Take 50 c. c. and dilute to about 100 c. c.; add calcium chloride solution in excess, and heat nearly to boiling, stirring vigorously all the while after the solution begins to cloud; apply the heat very cautiously towards the last, and continue stirring assiduously until a copious white precipitate of calcium citrate is formed and well coagulated. The precipitate will subside immediately. Filter; wash well with very hot water, first by decantation and afterwards on the filter. To the filtrate add ammoniac hydrate in very slight excess; add 15 grams of dry ammonium nitrate and precipitate the phosphoric acid with molybdic solution. Proceed as with total phosphoric acid.

Calcium chloride solution: This is a neutral 20 per cent. solution of calcium chloride.

It may be necessary to take an aliquot representing more than one-half gram on account of a small percentage of citrate soluble being present in the substance (less than 2 per cent.), thus necessitating the addition of a larger quantity of calcium chloride. The calcium citrate precipitate is somewhat bulky, but if large filters are used it will not prove too unwieldy and can be filtered and washed with great facility.

This process consumes very little time, and precipitation of the phosphoric acid with the molybdic solution can be accomplished within fifteen minutes after measuring an aliquot part of the filtrate obtained by treatment with ammonium citrate. Several experimental analyses of fertilizers have been made by this method, and all tests made by the above scheme have resulted satisfactorily. However, the limited amount of time employed in the examination of the subject has precluded a thorough investigation.

The following samples were subjected to analysis and the results given below verified by additional tests:

No. 1. South Carolina phosphate, sent by Professor Jenkins for the purpose of testing the Association method.

No. 2. Navassa phosphate, also from Professor Jenkins. In this sample, as shown by duplicate determinations, a portion of the phosphoric acid has reverted since our analysis was made last fall.

No. 3. Complete guano.

No. 4. Complete guano.

No. 5. Alabama phosphate rock.

No. 6. Phosphate containing a large percentage of citrate-soluble phosphoric acid.

Table of results.

	1.	2.	3.	4.	5.	6.
Total phosphoric acid	15.15	16.72	11.90	13.06	28.16	19.77
Soluble phosphoric acid	11.71	5.60	8.54	5.76	.....	.....
Insoluble phosphoric acid	1.15	5.48	1.09	3.46	25.84	2.21
Citrate-soluble by difference	2.29	5.64	2.27	3.84	2.32	17.56
Citrate-soluble by actual determination	2.30	5.76	2.21	3.77	2.43	17.35

B. B. ROSS,

Assistant in State Laboratory, A. and M. College, Auburn, Ala.

At 1 o'clock p. m. the Association adjourned to meet at 2 p. m.

AFTERNOON SESSION, TUESDAY.

The Association met at 2 o'clock, according to adjournment, Vice-President White in the chair.

The president introduced the Hon. Norman J. Colman, Commissioner of Agriculture, who spoke as follows:

GENTLEMEN: I return my thanks to you for the very cordial invitation extended to me to meet with you and to offer such suggestions as might seem suitable to me on such an occasion. It was an unexpected compliment, and I accept the invitation, not because I think I can offer any suggestions of any great value, but as an evidence of the deep interest I feel in the work in which you are engaged. I shall occupy your attention but for a very few moments.

The Association of Official Agricultural Chemists is an outgrowth of a meeting of chemists held in Washington five years ago for the purpose of considering the methods of analysis of fertilizers then in use. Since that time, as you well know, meetings have been held in Cincinnati, in Boston, in Atlanta, and at Philadelphia. While the membership of the Association is confined, I understand, to those engaged in official agricultural work, yet the meetings of the Association are open to all chemists, who are cordially invited to be present, to take part in the discussions, and contribute papers. Thus the scope of the Association is widened and its usefulness increased. In calling the late Convention of Agricultural Colleges and Experiment Stations which met here in July last, my object was to bring about co-operation between the Department of Agriculture and the various agricultural colleges and experiment stations of the country. I am well aware that the full value of all experimental work in agriculture can only be secured by subjecting it to careful chemical control. The character of the soil, the value of the fertilizers employed, and the nature of the products obtained can only be determined by careful chemical analyses. Without the knowledge which such analyses give, the agriculturist will be constantly groping in the dark, uncertain of his methods and doubtful of his results.

I understand that one of the chief objects of the present meeting is to discuss the methods now in use for the analysis of commercial fer-

tilizers. A few years ago the farmers of this country were ignorant of the existence of an artificial fertilizer. The natural fertility of our soil, the almost boundless extent of new lands open to pre-emption, and the cheapness of agricultural products rendered the use of artificial fertilizers unnecessary and expensive. But as scientific agriculture progressed, and unscientific agriculture became less remunerative, we were brought to see that a soil could not always give without receiving something in return. The agriculture which sought to retrieve, by extending its area, the losses which diminished fertility brought about soon proved to cost more than its returns. The scientific principles of crop growth and soil constitution, as first developed by Liebig, began to find a more general application. It was found that intensive was more remunerative than extensive agriculture. Thus the use of artificial fertilizers was gradually brought about by the combined influence of advancing science and diminishing farm receipts. From small beginnings the trade in commercial fertilizers has now grown until its value is more than $20,000,000 annually. It is thus seen that the interests which you are here to represent are by no means of small importance.

Speaking for the farmers of the country, I would say that they are heartily in sympathy with the object of your meeting. It is just as important to them, as buyers of fertilizers, as it is to the manufacturers of them, that some uniform method of analysis should be adopted. An analysis made in one State, by one method, and in another by another, cannot fail to be the source of constant misunderstanding between manufacturers and consumers. Let it be granted that the absolutely best method may not be devised, yet it is better that a less perfect method be uniformly employed than that the best method may be used in one locality and the poorest in another. In the late convention of scientific agriculturists steps were taken which look to the collection and publication by this Department of the results of scientific experiments in agriculture in all parts of the country. I need not impress upon you, in view of the probable success of this plan, the great importance of securing, in connection with such experimentation, uniform methods of chemical control. Thus, while I understand that your present meeting is to be devoted exclusively to the consideration of questions connected with the analysis of fertilizers, yet I cannot but hope that in future meetings you will discuss in general the methods of chemical analysis so that throughout the whole country perfect uniformity may be secured. Of great importance, also, it seems to me, in agricultural chemical analysis, is the examination of foods. It appears to me that it would be a proper function of this Association to fix standards of purity for the different kinds of food, and establish methods for the detection of adulterations which could be uniformly practiced and lead to harmonious results. For instance, in so simple a matter as the adulteration of milk, it would be hard to secure a conviction in a court of justice for any person practicing it, because of the absence of any official standard by means of which the extent of the adulteration could be meas-

ured. It should not only be the object of chemical control of agriculture that abundant crops should be produced, but also to see that the products of the fields should be delivered to consumers free of any cheap or deleterious adulteration. In the question of food adulteration I have long been greatly interested, and am anxious that some steps may be taken by means of which the extent of it can be diminished.

I have already directed the chemist of this Department to give attention to the adulteration of foods. The frauds that are practiced upon the public in adding cheap and frequently harmful ingredients to the food we eat, in order to make greater profits, ought to be exposed in no uncertain way, and the perpetrators of them held up before the public as objects of scorn and detestation. It seems to me that the members of this body, in their respective States, could do a useful and highly appreciative work in this direction by exposing the frauds that are practiced in adulterating the very necessaries of life. The purchasers of food need protection as well as the purchasers of fertilizers. I will go further and say that I think the General Government ought to cooperate with the respective State governments in passing the most stringent laws and using the most energetic means to punish those who are engaged in adulterating our foods or selling them after they have been adulterated. To such an extent is the adulteration of butter or the manufacture of a counterfeit article now carried on that the great dairy interests of our nation are almost prostrate. The honest producer of a pure article is impoverished, while the manufacturers of and dealers in a fraudulent article are enriched, some of them having become millionaires by this illegitimate work. The same may be said in relation to the adulteration of our sugars and sirups. Indeed, it is almost impossible to get a pure article of sirup in any market. The honest manufacturer stands no chance beside the unscrupulous one. Many an honest producer has become bankrupt in trying to keep up with his unscrupulous competitor. The road to riches seems to be not in the path of honesty, but in the great highway of rascality.

Mr. Chazal offered these resolutions:

Resolved, That the Association returns its hearty thanks to the honorable Commissioner of Agriculture for his instructive address, and for his courtesy in permitting the Association to use a room in the Department building.

Resolved, That the Commissioner is requested to furnish the secretary with a copy of his address to be spread upon the minutes.

Carried.

(*b*) ON POTASH.

The committee on potash made the following report:

METHODS OF ESTIMATING POTASH.

The first meeting of Agricultural Chemists, held in Washington July 28, 1880, recommended the following method of estimating potash:

Solution in water, removal of sulphates, phosphates, and magnesia by barium hydrate, clearing with oxalate or carbonate of ammonia, and precipitating with platinum chloride.

This method has at least the merit of brevity.

At the meeting of the same Association in Cincinnati, August, 1881, no action was taken with reference to potash.

At the Atlanta convention, May, 1884, Dr. Memminger described a method of determining potash given below:

Two to 2.50 grams of the fertilizer are weighed from a weighing tube into a beaker (capacity about 400 c. c.). In the case of ammoniated fertilizers, the fertilizer is first subjected to carbonization at a low temperature, when cotton seed or the like is present. To the material is added 5 c. c. of strong hydrochloric acid and then a little water. Heat is applied, and when the mass is at the temperature of 212° F., boiling water is added until the entire bulk will come to about 200 c. c.; to this is added a slight excess of barium chloride, and after a few minutes' boiling a strong ammonia is added until the mass is entirely alkaline. To this is then added first a slight (very slight) amount of milk of lime, then carbonate of ammonia in excess, and then a slight excess of oxalate of ammonia. The entire contents of the beaker are then brought to the boiling point and there kept for two or three minutes. After the mass has had time to precipitate the fluid is decanted, and after two decantations with boiling water (using 200 c. c. each time) the entire mass is thrown on a filter and washed three or four times with boiling water.

The filtrate is now evaporated in a porcelain dish over the direct flame of a Bunsen burner, and after the evaporation is carried to near the crystallizing point of the salts present a little strong ammonia is added, and then a few c. c. of oxalate of ammonia. The precipitate which now forms is thrown on a filter and the filtrate caught in a large crucible. After a sufficiency of washing the filtrate is evaporated very carefully until perfectly dry, and then the ammonium salts gotten rid of by ignition over a Bunsen burner. The carbonized mass contained in the crucible is moistened with 1 c. c. of very dilute hydrochloric acid (1 c. c. strong, HCl. to 4 c. c. of H_2O) dissolved in a little boiling water and filtered into a weighed crucible (porcelain). The mass is washed until there is no reaction with either litmus paper or silver nitrate, the contents of the crucible carefully evaporated until no more than about 2.5 c. c. remain in the crucible, and to this is added about 10 c. c. of 95 per cent. alcohol and 5 c. c. of standard bichloride of platinum solution. The precipitate then formed of bichloride of platinum and of potassium is allowed to stand overnight, and in the morning, after the crucible has been jarred to make the precipitate fall to the bottom, the supernatant liquid containing an excess of platinum solution is either poured off or else sucked up by means of a very fine pipette. (I have found this better and easier than decantation.) After three or four washings with alcohol (95 per cent.), using about 10 c. c. each time, the same process is employed for removing it, allowing time for each subsidence of the precipitate. The crucible is now placed in a steam bath, and the temperature kept at about 230° F. until the weight of the precipitate is constant. Of course the weight of the crucible subtracted from the weight of the crucible plus the precipitate dried at 230° F. gives the weight of the bichloride of platinum and potassium. In the case of kainite salts I employ the same plan of procedure, using, however, in the precipitations much less of ammonia and carbonate of ammonia, and seldom using oxalate. The original 2 or 3 grams, however, which is contained in my final filtrate after ammonium salts are gotten rid of, is, of course, brought to a definite bulk, and then an aliquot portion taken, so that I shall not have to use too great a quantity of bichloride of platinum.

Professor Noyes suggested the following improvements on the above plan:

I precipitate with platinum chloride in a small weighed beaker, evaporate, take up with alcohol, wash by decantation, pouring off through a small filter, then extract

the filter with hot water, washing into the beaker containing the main precipitate, evaporate to dryness and weigh. During this last evaporation it is advisable to add a drop or two of aqua regia to avoid reduction to metallic platinum.

Professor Stubbs said, speaking of the above method:

I use for washing potassic platinic chloride alcohol of 95 per cent. purity mixed with one-sixth of its bulk of ether.

Dr. Wiley gave his experience in the use of the Gooch crucible in potash determinations:

Mr. President, I have heard a great deal of discussion to day about estimating potash on a weighed filter. Now, sir, I think the use of paper filters in such estimation is a relic of barbarism. The perforated platinum of crucible, with its blanket of asbestus pulp, is to chemistry what the breech-loader and needle-gun are to war. The day of flint-lock muzzle-loading muskets and of weighed paper filters has passed. The Gooch filter is the great labor-saving machine of chemical industry. In potash determinations the double salt can be first dried and weighed. Then the salt is decomposed by ignition in a stream of hydrogen, the potassium chloride washed out, and the crucible dried and reweighed. Thus an easy and reliable check is placed on every determination.

At the same convention the committee on potash, consisting of Drs. E. H. Jenkins, W. J. Gascoyne, and H. W. Wiley, made the following recommendation:

That for the present nothing better could be suggested for the determination of potash than the plan adopted by the Washington convention.

The report was adopted.

At the Philadelphia meeting, September, 1884, the above committee on potash reported the following method, which was adopted:

Boil 10 grams of the fertilizer with 5 c. c. of strong hydrochloric acid and 300–400 c. c. of water for ten minutes. Cool the solution, and, without filtering, make it up to 1,000 c. c.; mix thoroughly and filter through a dry filter.

Take an aliquot corresponding to .5 or 1 gram; dilute, if necessary, to about 150 c. c.; heat to boiling, and precipitate the sulphuric acid with a slight excess of barium chloride solution. Without filtering add an excess of barium hydroxide, and heat again to boiling. Filter and wash, at first by decantation, till the washings are free from chlorides. Heat the filtrate nearly to boiling and precipitate the barium salts with ammonium carbonate and a little ammonia solution. Filter and wash, evaporate filtrat and washings to dryness, and ignite *below a red heat* till the amonium salts are removed and the organic matter is oxidized as completely as possible. The residue, consisting of chlorides of potassium and sodium, with some charcoal and possibly a little barium salt, which escaped precipitation, is digested with hot water, a few drops of ammonium carbonate are added, and the solution filtered and washed. The filtrate and washing are again evaporated to dryness and ignited gently.

The mixed chlorides are dissolved in water, an amount of platinum tetrachloride solution is added more than sufficient to form the double salt with all the potash and *soda* present, and the solution is evaporated at or below 100° C., so nearly to dryness that it becomes solid on cooling. To the cold mass 10 to 20 c. c. of strong alcohol (90 to 95 per cent.) are added, and the mass is well broken up with a stirring rod or pestle. After standing 5 to 10 minutes the supernatant liquid, which must have a reddish color from excess of platinum tetrachloride, is poured on a filter, more alcohol is added to the mixture of the double salts, and the whole stirred and pulverized and washed by decantation until the washings are perfectly colorless.

The precipitate is then brought on the filter by means of a wash bottle containing alcohol. The salt is dried at 100° C. and weighed. After weighing, the salt is dis-

solved from the filter with hot water, and the filter is dried and weighed together with any platinum which may have been reduced in drying down the solution with platinum tetrachloride or other impurities.

The actual potash is reckoned from the weight of the double chloride of potassium and platinum by multiplying by 0.19308.

Potassium chloride is reckoned from the double salt by multiplying by 0.3056. These factors are based on the following atomic weights:

Platinum	197.18
Potassium	39.13
Chlorine	35.46
Oxygen	16.00

At the same meeting a committee was appointed, consisting of H. W. Wiley, W. J. Gascoyne, and Clifford Richardson, to examine anew the subject of potash determination and report at the annual meeting of the society at Washington, September, 1885.

Glancing at the method used for estimating potash in fertilizers in other countries, the following points are brought to view:

The method in use in Germany twenty years ago for estimating potash in crude kainite is given by Stohmann.[1]

(1) Precipitation of sulphuric acid with barium chloride, separation of the magnesia by barium hydrate, precipitation of calcium and excess of added barium by ammonium carbonate, evaporation, and ignition, and final estimation of potash by platinic chloride.

(2) The liquid after treatment with barium chloride is evaporated to dryness with oxalic acid, the residue ignited, the chlorides dissolved in water, the magnesia filtered off, and the potash estimated with platinic chloride.

To avoid the repeated filtration the following method was employed:

(3) About 10 grams of the finely-powdered salt are treated with 300 c. c. hot water brought to a full boil and without minding the insoluble portion treated drop by drop with barium chloride. The barium sulphate settles rapidly, and, therefore, with care almost all excess of barium can be avoided. The whole, after cooling, is made up to 100 c. c., the volume of the precipitate having little influence on there sult.

It is now filtered, and 100 c. c. of the filtrate corresponding to one gram of the salt mixed with a solution of platinic chloride, which contains at least two grams of platinum. This is now evaporated to dryness on the water bath, treated with 80 per cent. alcohol, rubbed up with a glass stirring rod, and washed by decantation until colorless. The whole is then brought on to a weighed filter dried at 100° and weighed.

RESULTS OF METHOD.

A mixture containing 24.83 per cent. potassium sulphate gave, by method 1, 24.52 per cent. K_2SO_4; by method 2, 25.51 per cent. K_2SO_4; by method 3, 24.58 per cent. K_2SO_4.

It appears that treatment with oxalic acid tends to give somewhat

[1] Zeit. Anal. Chem., vol. 5, pp. 106 *et seq.*

higher results than are otherwise obtained, and this opinion is corroborated by some of the data to follow.

The use of oxalic acid to convert nitrates into carbonates was also suggested by Mr. Clifford Richardson.[2]

Nitrates are, after conversion into carbonates, readily obtained in the form of chlorides. It is doubtful whether a single evaporation with hydrochloric acid is sufficient to convert all nitrates present into chlorides.

G. Krause[3] gives the method in use a decade ago at Strassfurt for estimating potash. It is not greatly different from that described by Stohmann. The salt, after solution, is treated with the slightest excess of barium chloride, made up to a standard volume, and an aliquot part of the filtrate taken for the estimation. This is evaporated to dryness in a porcelain dish after treatment with an excess of platinic chloride. The residue is moistened with a few drops of water and then treated with 2 to 3 c. c. alcohol of 90 to 95 per cent., and well rubbed with a glass rod. It is then washed by decantation, and after having been dried at 120° to 130° weighed on a tared filter.

Since the potash of commercial fertilizers is derived almost exclusively from kainite, the fact that precipitated barium sulphate constantly incorporates the portion of the potassium chloride formed must not be lost sight of. It is true this loss is trifling, but at least its existence should be recognized.

West[4] has studied the disturbing effect of this substance and recommends the use of a factor for correction of results of a magnitude depending on the amount of sulphuric acid present. This is previously determined by titration with barium chloride and potassium chromate.

Ulex[5] recommends the use of a 20 per cent. glycerine solution in connection with the platinic chloride solution. For a mixture containing 0.5 gram potassium chloride he uses 5 c. c. of the glycerine solution and 10c.c. platinic chloride specific gravity 1.1. On evaporation the glycerine is left as a sirup, the crystals of the double salt are more perfectly formed, and much less alcohol is required for washing.

In 1880 Mr. R. R. Tatlock issued a circular in which he proposed to estimate potash in its salts as follows:

Take 35 grams of the sample, dissolve in water, filter and make up to 500 c. c. Place 10 c. c. of this solution in a small porcelain dish, add 20 c.c. water, and then 30 c. c. of the platinic chloride solution containing 7 grams platinum in 100 c.c. Evaporate on water-bath, but not to complete dryness, add a few drops of water, evaporate a second time, and treat the precipitate with 2 c. c. of the platinic chloride solution, stirring well. Bring the precipitate on a filter and wash it with 1 c.c. platinic chloride solution, and then wash dish, precipitate, and filter with as little 95 per cent. alcohol as possible. Dry the filter on the water-bath, transfer the precipitate as completely

[2] Am. Chem. Jour., vol. 3, p. 422.

[3] Arch. Pharm. 2, 407, 1874, and Zeit. Anal. Chem. 14, 184.

[4] Zeit. Anal. Chem. 1881, pp. 357 *et seq.*

[5] Zeit. Anal. Chem. 17, 175.

as possible to a small platinum dish, dry at 100°, and weigh. Incinerate the filter, which still contains traces of the precipitate, weigh the residue consisting of platinum and potassium chloride, calculate as K_2PtCl_6, and add to weight of salt found in platinum dish.

Zuckschwerdt[6] and West compared the results obtained by this method with those given by the method of Fresenius and a modified method of their own. Two determinations by the method of Fresenius gave 100.013 and 100.005 per cent., respectively. A mean of thirteen determinations of the same salt (chemically pure KCl), by Tatlock's method, gave 99.683 per cent. Nine determinations of the same by the author's modified method gave 100.023 per cent.

The radical defect of Tatlock's method is found in the solubility of potassio-platinic chloride in solutions of platinic chloride. In any case the method could only be used successfully in the absence of other acids than hydrochloric.

Following is an outline of the method employed by Zuckschwerdt and West:

Dissolve 10 grams of the sample in 500 c. c. of water, filter and take 20 c. c. of the filtrate. Add to this in a porcelain dish 7 c. c. solution of platinic chloride (7 grams platinum in 100 c. c). Evaporate to consistence of sirup with frequent stirring. By this means free hydrochloric acid is mostly driven off. After cooling add 10 c. c. 95 per cent., alcohol, wash with alcohol, on to a tared filter, dry at 110° to 115°, and weigh.

David Lindo[7] has made an extensive study of the estimation of potash as platinum double salt. When only sodium and potassium chlorides are present, he recommends the following method:

The sample dissolved in water should not contain more than 1 per cent. of the two salts. To this a solution of platinic chloride is added, containing by weight twice as much platinum as there are sodium and potassium chlorides present. Evaporate to dryness on water-bath and dry for two or three minutes. Cool and treat residue with 20 c. c., 98 per cent., alcohol, filter by upward filtration, and wash three or four times with small quantities of alcohol of the same strength as above. Rub the precipitate to impalpable particles in a little alcohol. Decant the alcohol, bring the precipitate on a tared filter, wash two or three times with alcohol, dry at 130°, and weigh. In nineteen experiments with mixed chlorides, in which the sodium chloride varied from 20 to 30 per cent. of the potassium, the mean of the potasium chloride obtained was 100.04 per cent. According to Lindo, K_2PtCl_6 is difficultly soluble in a half-saturated solution of amonium chloride. In the presence of sulphates, Lindo proposes to use a solution of ammonium chloride, previously saturated with platinic chloride. He experimented on a mixture of 65 parts potassium chloride, 25 parts magnesium sulphate, and 10 parts sodium chloride. As a mean of ten experiments he found that he had recovered 99.99 of the potassium. For full details of

[6] Zeit. Anal. Chem., 1881, pp. 185 *et seq.*

[7] Chem. News, 44, pp. 77, 86, 97, 129.

the work I refer to the original papers, which are too long for further quotation.

Dreyfus[8] has proposed another modification for the estimation of potash. Ten grams of the sample are incinerated after treatment with strong sulphuric acid. The ash is exhausted with hot water, the filtrate made up to 500, and 50 c. c. used for the potash determination by treatment with barium hydrate, filtration, and estimation with platinic chloride in the usual way.

An examination of the indirect methods of alkali estimation and of the disturbing influence of large quantities of sodium chloride on the direct estimation of potash as K_2PtCl_6 has been made by Dr. M. Kretschy.[9]

Interesting experiments in the estimation of potash in fertilizers may also be found in the report on the methods employed in the estimation of potash and phosphoric acid in commercial products prepared by Mr. A. H. Allen.[10]

Dr. R. Fresenius[11] discusses the factor which should be employed for converting K_2PtCl_6 into KCl. He concludes, after carefully examining the results obtained by the several proposed factors, that 100 parts of K_2PtKCl_6 dried to a constant weight at 130° contain 30.56 parts of KCl.

VOLUMETRIC ESTIMATION OF POTASH.

F. Moore[12] has proposed to estimate the potash in K_2PtCl_6 by fusing with double its weight of sodium oxalate, dissolving the mass in water and estimating the Cl volumetrically in the solution.

Koninck[13] has given a method of obtaining the whole of the chloride in a form easy of titration. He treats the hot aqueous solution of the K_2PtCl_6 with metallic magnesium. The platinum is precipitated with formation of magnesium oxide and escape of hydrogen. Titration is accomplished with silver nitrate, using potassium chromate as indicator.

M. Dubernard[14] has lately proposed a new process for volumetrically estimating potash.

This method consists in precipitating the potash salt acidified by nitric acid with titrated solution of chloroplatinate of sodium and afterwards estimating the excess of this solution by a solution of nitrate of silver with previous reduction of the platinum salt remaining in solution by zinc. By reason of the favorable double decompositions secured by the employment of the chloroplatinate of sodium, the method is applicable to all potassium compounds—carbonates, sulphates, chlorides, nitrates, phosphates, &c. A solution of 12 to 15 per cent. of chloropla-

[8] Bul. Soc. Chem., 38, p. 162.

[9] Zeit. Anal. Chem., 15, pp. 37 *et seq.*

[10] Chem. News, Vol. 35, Nos. 917 and 918, and Vol. 36, Nos. 920, 922, and 923.

[11] Zeit. Anal. Chem., 1882, pp. 234 *et seq.*

[12] Zeit. Anal. Chem., Vol. 12, 137.

[13] Revue Universelle des Mines, &c., Vol. 9, No. 2.

[14] Annales Agronomiques, Vol. 9, No. 7, p. 326 *et seq*

tinate of sodium in alcohol diluted with an equal volume of water is employed. On the other hand, a solution of silver containing from 12 to 15 grams of the nitrate per liter is used. Following is the method of titrating these solutions:

Of the solution of platinum 10 c. c. are taken in a flask holding 100 c. c.; to this is added a small portion of zinc powder, and the solution is boiled for a minute; all the platinum is then precipitated, and there remains in solution chloride of zinc and chloride of sodium. The volume is now made up to 100 c. c. with distilled water. The chlorides in one-half of the filtered liquid are then precipitated by the silver solution. Suppose it takes 40 c. c.; multiplying this number by 4 we have 160 c. c., which represents 20 c. c. of the solution of platinum.

Weigh out exactly 0.5 gram of a chemically pure salt of potassium, nitrate, or sulphate; dissolve this salt in a flask of 100 c. c. capacity, in a few c. c., of distilled water, add a little nitric acid, and then precipitate the potassium with 20 c. c. of the platinum solution; make the volume up to 100 c. c. with alcohol of 95 per cent., filter 50 c. c., reduce at a boiling temperature with a little powdered zinc, make up to 100 c. c.; the titration by the silver-salt obtained with the 50 c. c. of the filtered liquid (or 12 c. c. multiplied by 4 equals 48), subtracted from the original silver titration 160, will represent the chlorine precipitated in the state of chloroplatinate of potassium by 0.5 of a gram of the nitrate or sulphate of sodium; or 160 minus 48 equals 112 c. c., representing 0.5 of a gram of nitrate of potassium, or .232 of oxide of potassium. For the estimation of any potash salts whatever, proceed exactly in the way which has just been indicated, taking 10 c. c. of the solution of .5 grams of the sample in 100 c. c. The estimation of the chlorides pre-existing in the sample is to be made with the same silver solution (which must be titrated for this purpose), and the number of c. c. found for the half gram is to be subtracted from the titre of the silver-salt found after reduction by zinc.

Example.—Given 27 c. c. found after reduction by zinc, and 8 c. c. found in the half gram of the potash salt, then we will have $27 \times 4 = 108$, $108 - 8 = 100$, and $\frac{100 \times 0.232}{112} = 0.2076$ for 0.5 gram, or 41.52 per cent. of potassium oxide.

Dr. Wiley has had the above method carefully tried by Mr. A. E. Knorr, who finds that the difficulty of determining the end reaction makes the estimation of the chlorine very uncertain. He is now engaged in some modifications of the process, by means of which he hopes to reach a satisfactory degree of accuracy. The process, if it can be made reliable, is very quick and easy of application.

The committee believe they have collected in the foregoing notices all the chief processes of determining potash that have any novelty or promise of success. In addition they give some of the results obtained by the application of these principles and variations of them to the analyses of commercial fertilizers.

Dr. C. A. Crampton made at the request of Dr. H. W. Wiley a series of determinations of potash in a commercial fertilizer by the following methods:

(1) Two grams were taken, transferred to a filter, and washed with successive portions of cold water of about 2 to 3 c. c. each until the filtrate measured 100 c. c. The entire filtrate was then treated with an excess of barium hydrate in solution and allowed to stand on the water-bath for some time. A few drops of ammonium hydrate were then added, and a slight excess of a saturated solution of ammonium carbonate After standing on the water-bath for some time, the mixture was filtered, the precipitate thoroughly washed with hot water, and after the addition of hydrochloric acid filtrate was evaporated to dryness and ignited at a low red heat. The residue was treated with hydrochloric acid and water, filtered, the filtrate evaporated to dryness, and this operation was repeated until the residue showed little or no blackening on ignition. The residue was then dissolved in a small quantity of water, platinic chloride added in excess, evaporated nearly to dryness, treated with 80 per cent. alcohol, filtered on a Gooch crucible, the precipitate washed with alcohol, dried for two hours at 100°, and weighed. A mean of thirty determinations by the above method gave 2.19 per cent. of potash. (K_2O.)

(2) This method was exactly like the preceding, except that hot water was used for washing the samples instead of cold. A mean of 14 estimations gave 2.91 per cent. of potash. (K_2O.)

It is therefore evident that cold water is as effective as hot in extracting the potash from the samples by the above methods.

(3) The samples of fertilizers were first ignited to low redness. After the organic matter was thus destroyed the subsequent treatment was the same as above.

Seven determinations were made, the mean of which showed 2.56 per cent. of K_2O. This indicates that a portion of the potash was volatilized by ignition. It should be remembered, however, that the ignition was effected over an open flame and not in a muffle.

Two determinations made of the same sample of fertilizer as that used in the above experiments gave 3.07 per cent. and 3.00 per cent. K_2O, respectively.

Mr. W. P. Wheeler made six determinations with the same sample, first igniting in a muffle just to incipient redness, and, after moistening with HCl, proceeding as by the Washington method.

RESULTS.

	Per cent. of K_2O.
No. 1	3.06
No. 2	3.04
No. 3	3.05
No. 4	3.02
No. 5	3.02
No. 6	3.01
Mean	3.03

These results show that no potash was lost by the previous ignition, and the committee is of the opinion that previous ignition at a low temperature in a muffle can be practiced without the use of sulphuric acid and with great benefit to the subsequent manipulation.

The object of the comparative trial was to determine the magnitude of the error arising from adding the ammonium carbonate to precipitate excess of barium and separating the combined precipitate by a single filtration.

It appears from the above that the error amounts to 0.1 per cent. Perhaps by a very careful addition of the barium hydrate so as to have only the slightest excess for commercial purposes one filtration might be avoided.

Mr. Wheeler also made some determinations to compare the methods of double and single filtrations, with the following results:

After weighing the precipitate of K_2PtCl_6 in a Gooch crucible, it was reduced in a low red heat in a current of hydrogen, the potassium chloride washed out, and the resulting platinum weighed. The first column in the following table shows the percentage of K_2O calculated from the double chloride, and the second the same from the platinum.

First method.—Addition of barium hydrate in slight excess, filtration, precipitation of excess of barium by ammonium carbonate, determination of potassium in filtrate.

	Per cent. of K_2O	Per cent. of K_2O.
No. 1	12.26	12.30
No. 2	12.08	12.10
No. 3	12.22	12.16
Mean	12.12	12.19

Second method.—Addition of barium hydrate, and then, before filtering, of ammonium carbonate, filtering and proceeding in the usual way.

	Per cent. of K_2O.	Per cent. of K_2O.
No. 1	12.06	12.04
No. 2	12.04	12.02
No. 3	12.12	12.08
Mean	12.07	12.05

From the above it is seen that the error arising from a single filtration, as in the previous case, amounts to about 1 per cent. The percentage of potash calculated from the double salt is practically the same as from the platinum. Hence there appears to be no necessity for reducing the platinum in a current of hydrogen and a recalculation of the results. Dr. Crampton, working by his first and second methods, already described, obtained the following results with the same sample

that Mr. Wheeler used in the numbers just given. In the second column will also be found the results calculated from the reduced platinum.

	Per cent. of K_2O.	Per cent. of K_2O.
No. 1	10.23	10.17
No. 2	10.36	10.08
No. 3	10.14	10.02
Mean	10.21	10.09

From the same sample Dr. Crampton obtained, using the Washington method, as a mean of four analyses, 10.92 per cent. of K_2O.

The above results show that by reduction of the precipitated and hydrogen gas a reliable check on the accuracy of the analyses is obtained. But the numbers secured by reduction agree so closely with those got directly from the double chloride that for commercial purposes the additional work cannot be recommended.

The difference in the results obtained by the two experimenters above shows either the difficulty of getting even samples of the same fertilizer or that the magnitude of the personal equation is greater in the estimation of potash than it is for most other substances.

There is one precaution that should always be taken in potash determinations, viz, not to have any ammoniacal fumes in the room during the evaporation after the addition of the platinic chloride.

Illustrating the effect produced by this cause, six determinations of potash in a fertilizer in a room free of ammonia, and four others made in a room in which other analysts were working on the estimation of phosphoric acid, are given. The ten determinations were all of the same sample and were made by one person, namely, Mr. G. L. Spencer. The sample was of the same fertilizer as the one used by Messrs. Crampton and Wheeler as given above.

The per cent. of K_2O determined in room free of ammonia is in first column, and from room containing ammonia in second column.

	Per cent.	Per cent.
No. 1	3.03	3.17
No. 2	2.91	3.85
No. 3	2.94	3.65
No. 4	2.99	3.64
No. 5	2.93	0.00
No. 6	3.07	0.00

From a study of the above results it does not appear that any advantage is obtained from the methods employed to shorten the time and diminish the labor of a potash determination.

Six samples of fertilizers containing potash were prepared by the com-

mittee in as uniform manner as possible, and were sent in sealed packages to the members of the association.

Following is a description of the samples:

No. 1. Commercial kainite.

No. 2. Commercial superphosphate.

No. 3. Commercial high-grade phosphate, with nitrate of potash.

No. 4. Tankage and potash.

No. 5. Tobacco stems and ground bone.

No. 6. Ground bone and nitrate of potash.

Accompanying the samples the following circular letter was sent:

WASHINGTON, D. C., *July* 2, 1885.

SIR: In behalf of the committee on potash appointed by the Association of Official Agricultural Chemists at the Philadelphia meeting last September, I have sent you by express samples of fertilizers containing potash, numbered 1–6, respectively.

Will you determine in them water and potash by the method recommended by the association, and also by the method usually employed by you, or by any other method you may desire to try? When the work is done please report results to me with detailed accounts of methods employed other than that recommended by the Association. The names of the analysts are to be received by the chairman of the committee in strict confidence, and are not to be made known in connection with their results.

All the results received will, however, be tabulated and reported to each analyst contributing, that he may see how his work compares with that of other chemists. The greatest care has been taken to secure uniformity in the samples sent out. Inasmuch as the association will meet again in Washington early in September, it is desired that you forward the results of your work as soon as possible.

Respectfully,

H. W. WILEY,
Chairman Potash Committee.

Owing to the late date at which the samples were sent out, the committee has not received as many returns as had been expected.

In all, returns have been received from four laboratories, containing the results of the independent work of eight chemists.

These returns have been collected in two tables, the first of which gives the results of the analyses by the Philadelphia method, and the second by slight variations therefrom, explained in the subsequent notes.

Analyses of samples of commercial fertilizers by Philadelphia method.

Analyst.	(1) K_2O.	(2) K_2O.	(3) K_2O	(4) K_2O.	(5) K_2O.	(6) K_2O.
D	12.81	4.01	2.24	2.46	3.20	3.54
E	13.58	4.64	2.58	2.66	3.23	3.58
F	12.04	3.98	2.32	2.64	2.90	3.38
G	12.44	4.24	2.37	2.74	2.80	3.38
H	13.39	4.33	2.26	2.41	2.99	3.34
Mean	12.85	4.24	2.35	2.58	3.02	3.44

Determination of potash in committee's samples.

Analyst.	(1) K_2O.	(2) K_2O.	(3) K_2O.	(4) K_2O.	(5) K_2O.	(6) K_2O.
A	13.77	4.21	2 03	2.38	3.07	3.27
B	12.41	3.61	1.68	2.25	3.28	3.33
B′	12.03	3.45	1.76	2.27	3.23	3.47
C	14.24	4.23	2.48	2.29	3.55	3.59
F′	12.04	4.21	2.34	2.74	3.14	3.47
G′	12.80	4.47	2.54	2.61	2.90	3.38
Mean..	12.55	4.03	2.14	2.41	3.39	3.42

METHOD A.

Ignite sample at low red heat; exhaust residue with water, acidulated with hydrochloric acid; add barium hydrate; filter; precipitate excess of barium with ammonium carbonate; filter; evaporate; filtrate to dryness; ignite residue at low red heat; exhaust with water; filter; precipitate with excess of platinic chloride and proceed in the usual way.

METHOD B.

Take 2 grams of sample, digest on steam bath 15 or 20 minutes with 25 c. c. of water, transfer to a filter, wash with successive small portions of hot water until filtrate and washings amount to 100 c. c. The filtrate is treated with saturated solution of barium hydrate in slight excess, heated and filtered. To filtrate is added a little ammonium hydrate and then ammonium carbonate in slight excess, precipitate filtered off and washed, and the filtrate and washings evaporated to dryness and ignited. The dry residue is treated with a little hot water, filtered, a little hydrochloric acid added, evaporated to a thick sirup, treated with 80 per cent. alcohol, allowed to stand 12 hours, filtered through a Gooch crucible, dried at 105–110°, and weighed.

METHOD C.

Two grams of sampled boiled with 100 c.c. water and washed with 200 c. c. water on a small filter. Precipitate hot with 35 c. c. saturated solution of barium hydrate and filter. Add lump of ammonium carbonate to filtrate and heat until excess of carbonic acid has gone off. Filter off barium carbonate, add about half a gram of oxalic acid, evaporate to dryness in platinum dish, and ignite at a low red heat to destroy organic matter and nitrates. Filter on a 5-centimeter filter paper into a 50 c.c. platinum dish, add 2 c. c. dilute hydrochloric acid, then excess of platinic chloride, and proceed according to Crooke's select methods.

METHODS F′ AND G′.

These methods were the same as the one adopted in Philadelphia, with the exception that an ordinary filter paper was used instead of a Gooch crucible for collecting the precipitate.

After a careful consideration of all the results which have come to the notice of your committee, we do not think that the general princi-

ples of estimating potash should be greatly changed from those given in the report at the Philadelphia meeting. We therefore beg to suggest, for the consideration of the convention and for adoption for the forthcoming year, the following

METHOD FOR ESTIMATING POTASH.

In case the potash is contained in organic compounds like tobacco stems, cotton-seed hulls, &c., it is to be saturated with strong sulphuric acid and ignited in a muffle to destroy organic matter. Pulverize the fertilizer (200 or 300 grams) in a mortar; take 10 grams, boil for ten minutes with 200 c. c. water, and, after cooling and without filtering, make up to 1000 c. c. and filter through a dry paper. If the sample have 10–15 per cent. K_2O (kainite), take 25 c. c. of the filtrate; if from 2–3 per cent. K_2O (ordinary potash fertilizers), take 100 c. c. of the filtrate. In each case make the volume up to 150 c c., heat to 100°, and add, drop by drop, with constant stirring, slight excess of barium chloride; without filtering, in the same manner add barium hydrate in slight excess. Filter and wash until precipitate is free of chlorides. Add to filtrate 1 c. c. strong ammonium hydrate, and then, drop by drop, a saturated solution of ammonium carbonate until excess of barium is precipitated. Add now in fine powder 0.5 gram pure oxalic acid or 0.75 gram ammonium oxalate. Filter, wash the porcelain dish free of chlorides, evaporate filtrate to dryness in a porcelain dish, and, holding dish with crucible tongs, ignite carefully over the free flame below red heat until all volatile matter is driven off.

The residue is now digested with hot water, filtered through a 5-centimeter filter, and washed with successive portions of 2 c. c. water until the filtrate amounts to 30 c. c. To this filtrate, after adding two drops of strong hydrochloric acid, is added, in a porcelain dish, 10 c. c. of a solution of 10 grams of platinic chloride in 100 c. c. of water. The mixture is now evaporated on the water bath to a thick sirup, treated with 85 per cent. alcohol, well rubbed with the stirring-rod, washed with 85 per cent. alcohol by decantation, collected on a Gooch crucible, washed with 85 per cent. alcohol, afterwards with 5 c. c. ether, dried for 30 minutes at 100°, and weighed. It is not necessary to check the results by washing out the precipitate and reweighing the crucible, or by reducing its weight after washing out the potassium chloride. We recommend the continuance of the use of the factor 30.56 for converting K_2PtCl_6 to KCl, and 19.308 for converting to K_2O. We further recommend that the committee on potash which may be appointed for the coming year distribute at an early date samples of fertilizers to members of the association and others interested, with such recommendations as may seem best suited to secure a thorough trial of this and all new methods which may appear to promise success.

Respectfully submitted.

H. W. WILEY, *Chairman.*
W. J. GASCOYNE.
CLIFFORD RICHARDSON.

Prof. H. W. Wiley said on behalf of the committee, in presenting this report:

Mr. President, your committee, after having carefully considered the results of the analytical work done on the samples of fertilizers furnished by it to the members of this Association, have concluded that the plan recommended by the committee at Philadelphia, with a few modifications, should be continued during the coming year. The chief alterations which we propose, you will already have noticed, are the following:

(1) We recommend the abandonment of the use of hydrochloric acid in the preliminary digestion of the sample. All the potash salts in fertilizers which are likely to be of any use whatever to the growing plant are soluble in water, unless it be in the few cases, such as ground tobacco stems, cotton-seed hulls, &c., where we recommend a preliminary incineration with sulphuric acid. This will leave the potash in the form of sulphates readily soluble in water. We consider the preliminary use of hydrochloric acid as prejudicial. In the subsequent addition of barium hydrate the first portions of it are consumed in neutralizing the free hydrochloric acid present, and thus an amount of barium chloride is found in solution which will require a corresponding amount of ammonium carbonate afterwards to precipitate. As is well known, the precipitates of barium salts carried down with them traces of the potassium. It is true that the amount of potassium thus lost is not great, yet every method should be used which is possible to make it a minimum. It is for this reason, also, that the addition of barium chloride and of barium hydrate and of ammonium carbonate should be made, as indicated in the report of the committee, drop by drop, and in as slight excess as possible.

(2) The object of the recommendation to add a little oxalic acid or oxalate of ammonium is to facilitate the conversion of any nitrates of potash which may be present into carbonates on subsequent evaporation and ignition. By this means it appears to the committee that a single evaporation and ignition of the sample will be sufficient, and hence they have recommended that the second one, as proposed in the Philadelphia method, be abandoned. Subsequently, before the addition of the platinic chloride, we add two drops of hydrochloric acid, in order to convert any carbonates which may have been formed by the above process into chlorides.

(3) As will be seen in the report of the committee, numerous experiments show that the weight of K_2PtCl_6 obtained in the first instance, when the processes have been properly performed, is an entirely sufficient basis for the calculation of the percentage of potash present. Hence there seems to be no necessity for washing out the double chloride with hot water and reweighing, or for the reduction of the platinum in a current of hydrogen, washing out the potassium chloride, and reweighing the metallic platinum.

In respect of the factor to be employed, the committee do not feel warranted in recommending a change; they recommend, however, that the factor based on the new atomic weight of platinum as determined by Seubert, be given a thorough trial during the coming year, and the results be reported to the Association at its next annual meeting.

Dr. Jenkins said, referring to the potash committee's report:

The recommendation of the committee to dissolve potash in fertilizers without the use of acid is, I believe, very wise.

If acid is used in the extractive, there is a temptation, which some manufacturers have been unable to resist, to put in greensand marl, which may contain as much as 8 per cent. of potash, quite insoluble in water, and probably not readily available by plants. I believe no special precaution is necessary to separate N_2O_5 before making a potash determination, because most, if not all, is expelled in the usual method of procedure, as the following trials show: Two fertilizers having 2.96 and 1.38 per cent. of nitrogen in the form of N_2O_5 were treated as for the determination of K_2O, but instead of adding platinum chloride the concentrated solution was tested for N_2O_5 with negative results. .05 gram of KNO_3 was dissolved in water, NH_4Cl and $(NH_4)_2Cl_3$ were added, evaporated, and ignited.

The residue contained no N_2O_5.

25 gram of $NaNO_3$ with $1\frac{1}{2}$ equivalents of NH_4Cl (.888 grams) in solution was evaporated and ignited. In the residue was found chlorine equivalent to 96 per cent. of the nitrogen originally present which had been displaced by it.

A sample of acid rock had sufficient KNO_3 added to it to give 6.45 per cent. of N_2O_5 and 12.64 per cent. of K_2O. Taking no special precautions, on account of the nitric acid present a determination showed 12.72 of K_2O.

Mr. Gladding then read the following paper, which was ordered to be spread on the minutes:

ON THE ESTIMATION OF POTASH.

The standard method of estimating potash consists in evaporating the solution, which must contain the potash in the form of chloride, with excess of $PtCl_4$ solution, nearly to dryness, washing the residue with strong alcohol, and weighing as K_2PtCl_6.

A strongly advocated modification of the above is the method of Tatlock, the main feature of which is a preliminary washing with 2 or 3 c.c. of a strong platinum solution and final washing with alcohol. This method has the great advantage of estimating potash directly, whether in the form of chloride, sulphate, or nitrate.

In all the published experiments on the standard method we find a tendency to high results. Even when chemically pure KCl and NaCl are used without a mixture of other salts, and when the platinum solu-

tion has been refined to the utmost purity, this tendency to excess is recognized.

Thus Fresenius, in order to insure removal of all NaCl after washing with alcohol, recommends washing a few c. c. of water and recovery of any dissolved potash salt from the washings.

The committee of the British Association finds that in case the platinum solution is in large excess the results are 5 to 6 per cent. too high, and this even when chemically pure KCl alone is employed.

It is manifest that in many cases of commercial analyses where the contents of potash are unknown this large excess and consequent error cannot be avoided.

Again, it has been found that even when the platinum solution gives a blank experiment, a residue perfectly soluble in alcohol, it may, from presence of certain impurities, give results far too high when working with chemically pure KCl.

When, then, to the above considerations we add the conditions under which the process is used in commercial analysis, especially in fertilizer work, and the difficulty of removing all sulphuric acid, nitric acid, organic matter, lime, salts, &c., and obtaining a solution containing nothing but pure KCl and NaCl, the greater tendency to error is at once evident.

On the other hand, the fact that in Tatlock's method the potash can be estimated directly without removal of sulphuric or nitric acids is a strong argument in favor of its use, and were it not for the one objection—that there is a loss varying from 0 to .5 per cent.—we should certainly prefer it to the standard method.

The labor and great care required to make an accurate potash estimation by the standard method in fertilizer analysis has led to an examination of a method proposed by Lindo,* which seems to possess all the advantages of Tatlock's method, and at the same time to be free from a tendency to low results.

Lindo made 10 analyses of a mixture of KCl with 25 per cent. $MgSo_4$ and 10 per cent. NaCl.

This mixture was evaporated as usual with excess of platinum solution and the precipitate washed thoroughly with alcohol as usual, until all platinum salts except the potash salt has been removed.

A half saturated water solution of NH_4Cl was shaken in a bottle with K_2PtCl_6 till saturated with the latter.

This salt is very slightly soluble in the NH_4Cl solution and only a trifling amount is taken up.

This solution was used to dissolve out any Na_2SO_4 or chloride of the same bases from the precipitate.

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* Chemical News, xliv, p. 130, note.

A final washing with alcohol removed all NH_4Cl, and the Gooch crucible contained only pure K_2PCl_6. His results were as follows:

KCl taken.	Weight of precipitate.	KCl obtained.
0.46239	1.5148	100.11
0.40955	1.3404	100.02
0.42510	1.3920	100.07
0.41477	1.3597	100.18
0.45149	1.4797	100.16
0.48252	1.5805	100.10
0.44488	1.4552	99.96
0.48679	1.4244	99.66
0.48062	1.4050	99.71
0.41726	1.3649	99.96
		99.99

This proposed method was submitted to the following investigation:

Chemically pure KCl was obtained by recrystallizing chemically pure $KClO_3$, and fusing to convert it to KCl.

0.25835 g., if this KCl gave 0.4967 gAgCl, equal to 0.25836 gKCl.

5 c. c. of the platinum solution employed evaporated to dryness, dissolved perfectly in 90 per cent. alcohol.

A solution of KCl in water was now made. By weighing this solution the KCl employed in all subsequent experiments was very accurately determined. Using KCl alone, Lindo's method gave the following results:

KCl taken.	Weight of precipitate.	KCl obtained.
(1) 0.24618	0.80650	100.11
(3) 0.12752	0.41770	100.06
(3) 0.12395	0.40550	99.98

These analyses show that there is no tendency to loss by this method.

To test the method applied to the estimation of potash in the form of sulphate, chemically pure K_2SO_4 was employed, using an excess of platinum solution and several c. c. of HCl. The results were as follows:

K_2SO_4 taken.	Weight of precipitate.	K_2SO_4 obtained
(1) 0.12539	0.8580	100.95
(2) 0.13228	0.3790	102.81
(3) 0.49780	1.4148	101.45

These results show that with HCl alone added the ppt is not pure K_2PtCl_6. It may be that the presence of free H_2SO_4 causes the error.

To test this an amount of NaCl about equal to the K_2SO_4 was added in the following experiments, thus avoiding presence of free H_2SO_4:

K_2SO_4 taken.	Weight of precipitate.	K_2SO_4 obtained.
(1) ...0.134977	0.3782	100.01
(2) ...0.121427	0.3415	100.16
(3) ...0.122500	0.3429	99.95

The method was now applied to the estimation of potash in superphosphate, using the following mixture: To 60 parts of an acid phosphate were added 10 parts each of the following salts: $NaNO_3$, NaCl, $MgSO_4$ and $(NH_4)_2SO_4$.

A blank experiment, using 1 gram of this mixture, gave 0.08 per cent. potash.

This amount was deducted in subsequent experiments.

Experiment 1: 1 gram + 0.07484 gram KCl, containing 0.0478 gram K_2O, gave 0.2464 gram K_2PtCl_6. Taken, 4.78 per cent.; obtained, 4.75 per cent.

Experiment 2: 1 gram + 0.02748 gram K_2SO_4, containing 0.01485 gram K_2O, gave 0.01486 gram K_2O; taken, 1.485 per cent.; obtained, 1.486 per cent.

A second mixture, which was received from Dr. E. H. Jenkins, and which contained 12.62 per cent. K_2O by composition, gave by this method 12.61 per cent., 12.56 per cent., 12.63 per cent.

These very satisfactory results as regards accuracy, taken in connection with the far easier manipulation, have led to the adoption by our firm of the following scheme for the estimation of potash in fertilizers:

(1) *Superphosphates.*—Boil 10 grams of the fertilizer with 300 c. c. of water for ten minutes. Cool the solution, add ammonia in slight excess, thus precipitating all phosphate of lime, oxide of iron, and alumina, &c., make up to 500 c. c., mix thoroughly, and filter through a dry filter; take 50 c. c., corresponding to 1 gram, evaporate nearly to dryness, add 1 c. c. of dilute H_2SO_4 (1 to 1), and evaporate to dryness and ignite to whiteness. As all the potash is in form of sulphate, no loss need be apprehended by volatilization of potash, and a full red heat must be used until the residue is perfectly white. This residue is dissolved in hot water plus a few drops of HCl; 5 c. c. of a solution of pure NaCl (containing 20 grams NaCl to the liter) and an excess of platinum solution (4 c. c.) are now added, and the whole evaporated as usual. The precipitate is washed thoroughly with alcohol by decantation and on filter, as usual. The washing should be continued even after the filtrate is colorless. Ten c. c. of the NH_4Cl solution prepared as above are now run through the filter. These 10 c. c. will contain the bulk of the impurities, and are thrown away. A fresh portion of 10 c. c. NH_4Cl is now run through the filter several times (5 or 6). The filter is then washed thoroughly with chemically pure alcohol, dried, and weighed as usual. The platinum solution used contains 1 gram metallic platinum in every 10 c. c.

(2) *Muriates of potash.*—In the analysis of these salts an aliquot portion containing 0.500 gram is evaporated with 10 c. c. platinum solution plus a few drops of HCl. and washed as before.

(3) *Sulphate of potash, kainite, &c.*—In the analysis of these salts an aliquot portion containing 0.500 gram is taken, 0.250 gram of NaCl added, plus a few drops of HCl, and the whole evaporated with 15 c. c.

platinum solution. In this case special care must be taken, in the washing with alcohol, to remove all the double chloride of platinum and sodium. The washing should be continued for some time after the filtrate is colorless. 25 c. c. of the NH_4Cl solution are employed instead of 10 c. c., and the second 25 c. c. poured through at least six times to remove all sulphates and chlorides. Wash finally with alcohol, dry, and weigh as usual.

A single experiment attempting to estimate potash directly in nitrate of potash did not yield satisfactory results. In such cases it may be necessary to first evaporate to dryness with HCl and then proceed as in analysis of muriates.

To test the solubility of K_2PtCl_6 in the NH_4Cl solution prepared as above, 3.13 grams of finely pulverized K_2PtCl_6 were digested with 200 c. c. of the NH_4Cl solution and filtered through a Gooch crucible. The loss was found to be 0.0002 gram.

Wherever the standard method of estimating potash is employed, the washing of the precipitate of K_2PtCl_6 with the NH_4Cl solution would undoubtedly by a valuable addition to the present process.

To prepare the washing solution of NH_4CL, place in a bottle 500 c. c. H_2O, 100 grams NH_4Cl; shake till dissolved. Now pulverize 5 or 10 grams of K_2PtCl_4, put in the bottle, and shake at intervals for six or eight hours; let settle over night; then filter off liquid into a second bottle. The first bottle is then ready for a preparation of a fresh supply when needed.

Laboratory of Stillwell & Gladding.

THE ANALYSIS OF MANURE SALT.

At the request of some of the members, Mr. Gladding read some notes on the analysis of manure salt:

A sample of manure salt analyzed by us about a year ago tested 42.10 per cent. of potash. A second chemist making it over 43 per cent., a sample was sent to Dr. Jenkins for reference. He made it about 42.50. I wrote to him that we must agree better than that, and suggested that we repeat the work. The result of this further work was very curious. Though following the instructions adopted at Philadelphia most carefully, and doing the work personally, our results varied all the way from 42 to 43 per cent. We could neither agree with the other nor with ourselves. The only explanation I can give for this re-remarkable work is that I subsequently found that the manure salt contained a large amount of magnesia which was not precipitated by barium hydrate nor ammonium carbonate, but came down with the platinum precipitate and was only partially washed out by the 90 per cent. alcohol. By washing with NH_4Cl solution, however, this sample gave me accurately agreeing duplicates of 42.20 and 42.23 per cent.

Another very curious illustration of the errors liable to occur in the estimation of potash is the following:

I prepared a solution of platinum by precipitating on zinc, washing with boiling concentrated HNO_3, then dissolving in aqua regia, then evaporating to dryness to draw off free HCl. 5 c. c. of this solution evaporated to dryness dissolved perfectly in alcohol, but on testing chemically pure KCl with it I obtained 102 to 103 every time. But washing the solution with NH_4Cl solution, the impurity, whatever it was, was washed out, and the results came down to 100 per cent.; and further washing with NH_4Cl made no difference.

The Association adjourned at 4.30 p. m., to meet at 9 a. m. Wednesday.

MORNING SESSION, WEDNESDAY.

The Association reassembled at 9 o'clock, and was called to order by Vice-President White in the chair.

(*c*) NITROGEN.

Mr. Chazal made an oral report for the committee on nitrogen. In the absence of the other members of his committee he requested that another committee be appointed on the report of the committee on nitrogen and on the method to be used in determining nitrogen during the next season. It was so moved and carried.

Committee, Chazal, Jenkins, and Wiley.

In the course of the discussion of methods of determining nitrogen, Professor Wiley said, with regard to

THE KJELDALH METHOD:

Mr. President, it is probably true, as Daffert has suggested, that in the estimation of nitrogen by Kjeldalh's method the process goes on in the following way:

(1) The sulphuric acid abstracts water from the organic compounds.

(2) The sulphurous acid produced by the action of the carbonaceous mass formed by the dehydration of the organic substance has a reducing effect upon the nitrogenous bodies present.

(3) The decomposition products containing nitrogen which are finally formed are converted into ammonium compounds by the energetic oxidation produced by the permanganate of potassium. It is probable, however, that the use of this latter reagent is not absolutely necessary; but without it the duration of the heating with sulphuric acid and anhydrous phosphoric acid must be continued somewhat longer.

Dr. Jenkins has already called attention to the error which is produced in distilling the alkaline mass with zinc, due to the fact that the liberated hydrogen carried over a portion of the alkali mechanically. Pfeiffer and Lehmann recommend a simple apparatus to prevent this mechanical transportation of the alkali. They interpose in the path of the distillation tube a platinum comb surrounded with fragments of

glass, which they claim stops and holds the alkali. It is also possible that if the alkali employed contained a trace of nitrate, the action of nascent hydrogen upon it would result in the formation of ammonium, and thus a total amount of ammonia obtained might be greater than that in the original sample. The method of Wilfarth, as already suggested by Dr. Jenkins, does away with the necessity of the use of zinc. By the addition of mercury the time required for heating with the sulphuric acid in some cases was reduced to thirty minutes. Wilfarth states that only in one case was he troubled by the bumping of the liquid during distillation, and never when potassium hydrate is used instead of sodium.

(2) *METHODS TO BE USED DURING THE NEXT YEAR.*

On motion of Professor Wiley the report of the phosphoric acid committee was approved and the method and recommendations proposed by them were adopted.

Dr. Dabney moved that the next committee on phosphoric acid be instructed to request the chemists to whom they send test samples to make the determinations of water soluble and citrate insoluble (citrate soluble indirectly) during a particular week to be named by the committee. Carried.

On motion of Mr Chazal the report of the potash committee was approved and their method and recommendations were adopted for the next season.

Prof. F. W. Clark, by request of the members, gave a brief discussion of the atomic weight of platinum.

He said, in addition, that he washed the Pt_2 preciptate on an ordinary filter and washed it through into a Pt capsule, in which it can be dried at any temperature.

The committee on the report on nitrogen submitted the following, which was adopted:

The committee appointed to consider the report of the committee on nitrogen beg to report that the returns from the samples sent out by the committee were so few and meager and the discrepancies so large as to make it inadvisable to recommend any method for the determination of nitrogen for use during the next season, and recommend that the entire report of the last committee be referred, without further action, to the next committee on nitrogen.

P. E. CHAZAL,
Chairman.
E. H. JENKINS.
H. W. WILEY.

This report was adopted.

Professor Wiley said, in this connection:

Mr. President, I suggest to the next committee on nitrogen that in sending out samples for analysis during the next year they include

some of chemically pure compounds in which the percentage of nitrogen is definitely known, and that they suggest to the analysts receiving the samples that they first try their apparatus, reagents, and chemicals on these known samples before beginning with the unknown. Having proved the reliability of their manipulation they will be better satisfied with their results obtained on bodies of unknown composition. I suggest also that the same course be followed by the other committees of the Association.

Dr. Dabney added to this suggestion that the committee send out for test analyses selected organic nitrogen compounds of well-determined composition and which can be obtained in perfect purity (well crystallized), to represent various per cents of nitro genin its several relations in amido, imido, nitro, nitrose, and cyanogen, &c., compounds.

(3) ELECTION OF OFFICERS.

Mr. Chazal moved that a committee of three be appointed to nominate officers for the next year, under article 3 of the constitution.

Carried; and Chazal, Stubbs, and Wiley appointed the committee.

This committee reported the following nominations:

For president, Prof. H. W. Wiley.

For vice-president, Dr. Charles W. Dabney, jr.

For secretary and treasurer, Clifford Richardson.

For members of the executive committee, W. J. Gascoyne and Prof. H. A. Houston.

These officers were duly elected for the ensuing year.

The Chair appointed the following standing committees:

(1) On methods of determining phosphoric acid:
Prof. H. C. White, of Georgia;
Dr. E. H. Jenkins, of Connecticut; and
Prof. William C. Stubbs, of Louisiana.

(2) On methods of determining nitrogen:
Dr. C. W. Dabney, jr., of North Carolina,
Prof. J. A. Myers, of Mississippi, and
Prof. W. E. Moses, of Tennessee.

(3) On method of determining potash:
Prof. W. J. Gascoyne, of Virginia;
Mr. Clifford Richardson, of Washington; and
Prof. N. W. Lord, of Ohio.

(4.) *MISCELLANEOUS BUSINESS.*

Dr. Dabney, referring to article 1 of the constitution, which declares it is one object of this Association "to secure as far as possible uniformity in legislation with regard to the regulation of the sale of commercial fertilizers in the different States," moved that the Association request

Mr. A. De Ghequier, secretary of the National Fertilizer Association, to express to them his views on this subject.

Carried.

In response, Mr. De Ghequier said:

Mr. President and gentlemen of the Convention, the discussion as regards the new way of expressing analysis requirements on bags in the State of Alabama affords me a welcome opportunity to lay before you two requests which the two associations I have the honor to represent delegated me to respectfully submit to your earnest and favorable consideration.

Both requests have reference to that part of article 1 of your constitution which says that its object is to secure, as far as possible, uniformity in legislation with regard to the sale of commercial fertilizers in different States. Concerning the further object consisting in securing uniformity and accuracy in the methods and results of fertilizers analyses, the beneficent influence of your Association has already been felt in a marked degree. The adoption of the method of analysis which your Association recommends from time to time for the determinations of the valuable constituents of a fertilizer by all State chemists has been followed by much closer agreement in results, so that the trade feels that the question of still further narrowing down the margin of discrepancy is perfectly safe in your hands. Instead of preferring complaints on this subject, the trade desires me to thank you for the energetic and efficient way in which your Association has dealt and continues to deal with the analysis question which has been in the past a source of great deal of trouble and dissatisfaction. While there are still differences, greater than manufacturers think should exist, the improved status of the situation justifies the expectation that by and by the attainable amount of accuracy will be obtained.

But as regards "uniformity of legislation" the two associations appeal to your services with the confident hope that you will be pleased to render us the assistance asked for, because we think that what we desire is reasonable, just, possible, and advantageous to all concerned—trade, consumer, and Department of Agriculture.

The first request is, that your Association will decide upon *one* mode of expressing analysis requirements; the second, that your Association recommend to the respective departments to have *that* nomenclature supersede the present discordant phraseologies in the respective laws.

The reasons which prompt such request are forcibly brought out by the recent change in the Alabama law. A change in the mode of expressing analysis requirements necessitates a change in the branding of bags—that is to say, whatever stock of bags a manufacturer may have on hand branded, as the Alabama law required them to be branded last season, is not available this season. And inasmuch as manufacturers avail themselves of the advantages invariably resulting from con-

tracting for large quantities, they order bags in lots of tens of thousands at one time. Rebranding is an expensive process and entails a remaking, besides a fresh printing. Any change consequently is accompanied by a direct loss to the manufacturer, proportioned to the amount of unused new bags on hand from a previous season. Nor is this all.

As you are all aware, fertilizers are stored in bulk at ports and other distributing centers and the bagging, &c., is attended to by the forwarding departments of the various transportation lines. This operation is thus entirely beyond the manufacturers' control. With the multiplicity of bags at each of these points, it may and does happen that an order for a shipment in one State is filled in bags destined for another State, and in that case the manufacturer is held responsible for a violation of the law and incurs the penalties. Thus a mistake for which he is in no way responsible works an extreme and unjust hardship for no other reason than this, that the mode of expressing the contents of phosphoric acid, ammonia, and potash differs in the two States. For this difference no sufficient reason does exist.

You are all agreed that phosphoric acid, ammonia, and potash are the valuable elements of fertilizers, and that the contents of these constitute its value to the farmer. What is gained by compelling a manufacturer to print on the bags of one State "ammonia, actual and potential," and in another "ammonia, or its equivalent in nitrogen"? By agreeing upon one nomenclature for all States, or at least groups of States, this whole difficulty would be overcome, and the manufacturer would be able to sell the same fertilizer in one and the same bag in all States or certain groups of States at least, whereas now he is compelled to run a constant risk on account of the diversity of bags. Decisions in the supreme court of Georgia and in other States furnish ample evidence that this risk is not fictitious, but exposes sometimes manufacturers to an unjust loss of large sums. The Association does not express any preference for one nomenclature over another, but is perfectly willing to conform to any you may adopt. If it is desirous to have the same as plain and intelligible to the farmer as is consistent with due regard for scientific terminology, it expresses a desire which you, no doubt, indorse in every way, since your efforts are directed to educate the farmer to a proper understanding of the analysis.

Now, as regards the second request, it is made simply because the trade well knows that any change in the fertilizer law, unless properly indorsed by the agricultural departments, has little chance of being passed, hence the co-operation and assistance of the several departments is essential. On a question, however, which falls so entirely into the province of chemists as the proper phraseology to be used for expressing analysis requirements on bags, our Associations are convinced that a decision of your body will receive everywhere the consideration it is entitled to. Your recommendation of one mode of nomenclature is, therefore, pretty sure to be favorably indorsed by the several gen-

tlemen who preside over the agricultural departments, and promises thus a much needed relief.

Whether this whole subject requires a special committee's labor or not, is a question for you to decide.

Permit me, in conclusion, to thank you for the time you have allowed me to put before you the requests of our Association, and to express the conviction that you will be pleased to take such measures as will provide in an effective manner relief. With these remarks the associations I represent intrust their interests to your safe keeping."

Mr. Chazal moved that acommittee of three be appointed, with vice-president White as chairman, to consider the question of uniformity of legislation and regulations as to the inspection of fertilizers, and to prepare a draft of a uniform law to be submitted to the convention which it is expected will be held at Washington to consider the matter.

Carried.

Committee, White, chairman; Chazal and Dabney.

Mr. Chazal moved that article 6 of the constitution be changed to read as follows:

> The annual meeting of this Association shall be held at such places as shall be decided by the Association and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

Carried.

On motion of Professor Wiley, Washington, D. C., was selected as the place for the next annual meeting.

On motion of Mr. Gascoyne, the secretary was instructed to notify all chemists entitled to membership in this Association of the aim and work of the Association, and to write them to take an active part in it.

The secretary announced that since the assembling of the Association he had received a letter from Dr. Robert Peter, State chemist, of Lexington, Ky., accepting membership in the Association and expressing regret at his constrained absence from this meeting.

At 1 p. m. the Association adjourned sine die.

CHARLES W. DABNEY, Jr.,
Secretary.

H. C. White,
President pro tem.

APPENDIX.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, ADOPTED AT PHILADELPHIA SEPTEMBER 9, 1884.

I. This Association shall be known as the Association of Official Agricultural Chemists in the United States. Its object shall be to secure, as far as possible, uniformity in legislation with regard to the regulation of the sale of commercial fertilizers in the different States, and uniformity and accuracy in the methods and results of fertilizer analysis.

II. Analytical chemists, connected with departments of agriculture, State agricultural experiment stations and State boards, exercising an official fertilizer control, shall alone be eligible to membership; and one such representative from each of these institutions, when properly accredited, shall be entitled to a vote in the Association. All analytical chemists and others interested in the objects of the Association may attend its meetings and take part in its discussions, but shall have no vote in the Association.

III. The officers of the Association shall consist of a president, vice-president and secretary, who shall also officiate as treasurer; and these officers, together with two other members to be elected by the Association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board, whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee to continue in office till the annual meeting next following.

IV. There shall be appointed by the chair, at the regular annual meeting, three standing committees, of three members each, to be called respectively, the Committee on Phosphoric Acid, the Committee on Potash, and the Committee on Nitrogen. It shall be the duty of these committees to test methods, to distribute samples to members of the Association and others who may signify their desire to participate in the work, and to present a written report at each annual meeting embodying the progress made during the year in analytical methods bearing on their respective topics, and the results of work done under their direction.

V. The special duties of the officers of the Association shall be further defined, when necessary, by the executive committee.

VI. The annual meeting of this Association shall be held at such place as shall be decided by the Association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

VII. Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, a majority of members shall constitute a quorum.

VIII. The executive committee shall confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the Association.

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